PB87-129540

Phase Distributions of Low Volatility Organics in Ambient Air

SRI International, Menlo Park, CA

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Dec 86

U.S. Department of Commerce
National Technical Information Service
NTIS

PB87-129540

EPA/600/3-86/064
December 1986

PHASE DISTRIBUTIONS OF LOW VOLATILITY ORGANICS IN AMBIENT AIR

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Contract 68-02-3748

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RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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TECHNICAL REPORT DATA *(Please read Instructions on the reverse before completing)*		
1. REPORT NO. EPA/600/3-86/064	2.	3. RECIPIENT'S ACCESSION NO. PB87 129540/AS
4. TITLE AND SUBTITLE PHASE DISTRIBUTIONS OF LOW VOLATILITY ORGANICS IN AMBIENT AIR		5. REPORT DATE December 1986 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Bruce K. Cantrell, Louis J. Salas, Warren B. Johnson and James C. Harper		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS SRI International 333 Ravenswood Avenue Menlo Park, California 94025		10. PROGRAM ELEMENT NO. CDWA1A/01 - 2045 (FY-86) 11. CONTRACT/GRANT NO. 68-02-3748
12. SPONSORING AGENCY NAME AND ADDRESS Atmospheric Sciences Research Laboratory-RTP, NC Office of Research and Development U. S. Environmental Protection Agency Research Triangle Park, North Carolina 27711		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/09
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 81
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (9-73)

NOTICE

The information in this document has been funded by the United States Environmental Protection Agency under Contract No. 68-02-3148 to SRI International. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Current strategies to control photochemical air pollution rely on abating the emission of volatile organic compounds. Primarily, these compounds exist in the vapor phase, and are those with a carbon number of ten or less. Recent attention has been given to low-volatility organic compounds (LVO) which may be partitioned between the gas and aerosol phases, and may only partially participate in smog formation. A three-part study was conducted to determine the role of such LVO's. First, a comprehensive review was made of the existing literature on atmospheric LVO to evaluate existing data and the measurement techniques used to collect the data. Second, an effort was made to develop an "estimator" for the phase distribution of LVO's in the atmosphere. While exact theoretical calculations of LVO adsorption on ambient surfaces are difficult, estimation based on the phenomenology is possible. This semi-empirical calculation has been applied to the n-Alkane series with some success.

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ACKNOWLEDGEMENTS

The authors wish to thank Louis J. Salas for his expert technical assistance, and Richard Brodzinsky for his efforts in the original literature search. The Environmental Protection Agency Project Officer, Robert Arnts, made a number of helpful suggestions in the preparation of this final report.

I INTRODUCTION

Current strategies to control photochemical air pollution rely on abating the emission of volatile organic compounds. Primarily, these compounds are those with a carbon number of ten or less. Recent attention has been given to low-volatility organic compounds (LVO), which may also contribute to smog formation. To determine the role of such LVOs in smog formation, both the reactivity and the phase distribution of each compound must be known.

When these organics are emitted into the atmosphere, they can exist in either the gas or aerosol (solid/liquid) phase. Under ideal conditions, the compounds will eventually vaporize and reside solely in the gas phase until the partial pressure of the compound exceeds the vapor pressure of the pure compound. In the "real world," however, LVOs are phase distributed not only by the pure substance's thermodynamic properties, but also by the adsorption and retention properties of the myriad different surfaces which exist in the atmosphere. These include both water droplets and atmospheric aerosols. Most of these surfaces are, of themselves, extremely complex and poorly understood.

To deal with this problem, this study was conducted in three parts. First, a comprehensive review was made of the existing literature on LVO. This review covered both an evaluation of existing data on atmospheric LVOs, and the measurement techniques used to collect the data. Following this, a selection was made of the n-Alkane compounds for the study to focus upon. These compounds were selected because they represent a uniform compound structure type covering a wide range of carbon numbers.

In the second part of the study, an effort was made to develop an "estimator" for the phase distribution of LVOs in the atmosphere. While exact theoretical calculations of LVO adsorption on ambient surfaces are nearly impossible, estimation based on the phenomenology is possible. This semi-empirical calculation has been applied to the n-Alkanes with some success.

The third part of the study was conducted concurrently with the other two. In this portion of the study an attempt was made to develop and test an improved and reliable collection and analysis technique for determination of the phase distribution of low volatility organics in ambient urban air. Each portion of the study is discussed separately in this report.

II LITERATURE REVIEW AND EVALUATION OF PUBLISHED DATA

Review of the literature on low-volatility organic compounds covered three general areas: reports of measurements in the atmosphere of both gas phase and aerosol concentrations, review of the sampling techniques used to obtain these measurements, and review of the attempts at systematic analysis of the phase distribution data. These areas are discussed in the following subsections.

A. Measurements of LVO in the Atmosphere

In the past decade a considerable amount of effort has gone into assessing the aerosol/gas phase distribution of low volatility organics in the atmosphere. All of these sampling and analysis efforts use a filter to remove aerosol from the sample air followed by a gas phase trap to remove the organic vapor. It is convenient to divide the literature in this work into two groups of papers. The first group is that work which ignores aerosol sample loss from the filter due to vaporization and subsequent enhancement of gas phase material on the trap medium. The second group consists of those measurements in which attempts were made to either correct the measurements for these effects, or to conduct the sampling in such a manner that they would be negligible.

The first group includes work by Della Fiorentina et al (1975 a,b), Cautreels and Van Cauwenberghe (1976, 1978), and Eichmann et al (1979, 1980). Della Fiorentina and Cautreels in their first efforts concentrated on laboratory analysis of collected aerosol for organic compounds. Della Fiorentina, used infrared spectometry as an analytical technique, while Cautreels used high resolution gas chromatography-mass spectroscopy. Results of these measurements for atmospheric aerosol included reports of concentrations for over one hundred separate compounds. The list included the n-Alkanes and simple polyaromatics such as benzo(a)pyrene. Because no attempt was made to correct for sampling

losses, these early measurements yielded atmospheric confirmation of existence and order of magnitude concentrations of the organics in these atmosphere. In their later work, Cautreels and Cauwenberghe (1978) attempted to investigate sampling losses, and to provide estimates of the phase distribution between aerosol and gas phase in urban air for many of the compounds detected. Most notable among these were the aliphatic hydrocarbons. Since this family of similar compounds has a progressively lower vapor pressure as the carbon number increases, it provides a convenient series of test compounds. These can be used to check the measurement techniques for systematic sampling effects associated with volatility. They also provide a series of compounds that can be used to measure the effect of volatility on the aerosol/gas phase distribution of LVO in the atmosphere. Results indicate that n-Alkanes with carbon numbers less than 18 are entirely in the gas phase, and those with carbon numbers greater than 22 had 50 percent of the sample in the aerosol phase. Since no attempt was made to correct for material loss during sampling, the latter conclusion is suspect. Eichmann et al (1979, 1980) conducted measurements of n-Alkanes in two remote locations: on the west coast of Ireland and at the Australian Clean Air Baseline Station, Cape Grim, Tasmania. Their results were similar to the 1978 measurements by Cautreels and Van Cauwenberghe in that below carbon number 18 the fraction of the LVO in the aerosol phase was less than 2 percent, and from carbon number 26 up, the fraction was approximately 50 percent. Again, because no attempt was made to assess the effect of material loss from the filter, the results should only be considered as qualitative. The results from this group of papers give trends for the phase distribution of LVO in the atmosphere, but cannot be used as quantitative measures of the phase distribution.

The second group, those measurement efforts that make some attempt to adjust for sample loss, are represented by papers by Broddin et al (1980) and Van Vaeck et al (1984). Although Broddin et al, made no attempt to correct their measurements, they sampled aerosol in such a way that it minimized the amount of air passing through the filter after aerosol was collected. They did this manually by dividing the aerosol

sample into small fractions of the total. In this way, sample loss was limited to less than 20 percent of the sample. Van Vaeck et al sampled for the aerosol phase in a similar manner, using an automated sampler that changed filters ten times each day. This minimized the amount of gas phase artifact originating with the filter material. Van Vaeck also evaluated the loss of 'blow-off' contributions of a Hi-Vol cascade impactor sampler and Hi-Vol filter. This permitted correction of the aerosol phase organic concentrations measured, and a reasonably accurate determination of the aerosol/gas phase distribution for the n-Alkanes for a wide variety of locales and atmospheric conditions; e.g., urban and rural concentrations as a function of seasonal change.

The data developed by these two groups of investigators has been used in Section III of this report for detailed comparison with the results of theoretical calculations of the phase distribution for the n-Alkanes as a function of locale and season, and will not be discussed here. However, some general conclusions reached by the authors concerning n-Alkanes in the atmosphere can be summarized as follows:

- n-Alkanes with carbon numbers below 18 reside entirely in the gas phase. The exception to this is for an urban sampling location in winter. Under these conditions the fraction of these LVO compounds in the aerosol phase may approach 10 percent.
- The aerosol/gas phase distribution of n-Alkanes in the atmosphere is highly seasonal and locale dependent. As one progresses from summer to winter, the fraction of the LVO in the aerosol generally increases. The carbon numbers of n-Alkane that are essentially 100 percent aerosol decrease from $>C_{24}$ to C_{20}.
- There is a marked particulate preference for odd carbon number hydrocarbons, presumably as a result of natural emissions.
- The aliphatic acids show the same general pattern as the normal alkane series, with the odd carbon number compounds predominantly in the particulate phase.
- Simple polyaromatic hydrocarbons (PAH) and alkylated PAH (except naphthalene and alkylated naphthalenes), are distributed between the aerosol and gas phases. Again, there is a general correlation between increasing molecular weight and increasing particulate/gas phase distribution. In the analysis, several

isomers concentrations were combined, making it impossible to observe a carbon number or ring size preference. Anthracene and phenanthene (3-ring isomers) are predominantly in the gas phase. Benzopyrene and coronene are only found in the particulate phase: gas phase detection level <0.008ng m^{-3}, Miguel and Friedlander (1978).

- Phthalic acid esters are predominantly, or exclusively, gas phase species.

B. Sampling and Techniques

Several sampling methods have been used. Cautreels and Van Cauwenberge (1976, 1978) and Broddin (1980) collected aerosols on glass filters, and gas phase organics on a Tenax sorbent trap downstream of the filters. The maximum volume of air sampled by this method is 2700 m^3/g at 20 degrees C. Other work by Bertsch et al (1978) with Tenax shows a selectivity towards certain classes of compounds; high molecular weight compounds were more easily retained than low molecular weight substances. Storage times of four months did not reveal any apparent changes. Work by Duce and Gagosian (1982) on atmospheric alkane distribution compared vapor samples using 3 different sorbents. The samples were taken at different locations, so the absolute values cannot be compared, but the sorbents effectively tapped n-Alkanes.

Tenax	C10 - C17
polyurethane foam plugs	C17 - C28
polyurethane foam plugs	C23 - C30
florosil	C13 - C17

It would seem that the carbon number ranges are indicative of the collection efficiences of the sorbents. Another method, used by Miguel and Friedlander (1978) used quartz collection discs for the aerosols and a cold trap for the vapors.

C. Description of Atmospheric Phase Distribution

The most recent attempt to explicitly describe the aerosol/gas phase distribution of LVO material in the atmosphere in a systematic manner is that by Junge (1977). His analysis was based on the theoretical description of the adsorption of gases on environmental surfaces by Brunauer et al (1938). This so-called "BET" theory permits estimation of the fraction of the total atmospheric LVO in the aerosol phase. The theory was compared with the data of Eichmann et al (1979) by Hahn (1980). While the result was not convincing, the basis for the analysis is well founded. As a result we have used the BET theory in Section III of this report as the basis for the development of an estimator for the aerosol/gas phase distribution in the atmosphere.

III ESTIMATOR FOR PHASE DISTRIBUTION OF LVO IN AMBIENT AIR

A. BET Theory Estimator

In developing an estimator for the fraction of ambient LVO found in atmospheric aerosol, it is important to consider the mechanism by which the vapor is incorporated into ambient aerosol. Most organics emitted into the atmosphere are initially in the gas phase. These then undergo both homogeneous and heterogeneous condensation as the emission gas is diluted and cooled. A description of this process was given by Hidy and Brock (1970). As the aerosol/gas phase mixture moves away from the source, an equilibrium is reached in mass exchange between the gas and aerosol phases. Subsequent aerosol growth is controlled by coagulation and deposition processes. The aerosol/gas equilibrium phase distribution will change in response to dispersion of the mixture in the atmosphere. The resulting redistribution of the organic components of the aerosol has been termed aerodynamic elution by De Wiest and Della Fiorentina (1975), and essentially is a result of dilution of the aerosol/gas mixture.

The LVO aerosol/gas equilibrium is controlled by the gas phase concentration, the distribution of LVO in the aerosol, and the concentration and condition of the aerosol surface. These parameters are critical in treating LVO phase equilibria in the atmosphere. Previous data on urban aerosol indicate that although most atmospheric aerosol are an internal mixture of compounds in water, mass transfer of these compounds occurs at the surface of the aerosol, Whitby (1981) and McMurry and Friedlander (1979). As a result, aerosol/gas exchange of compounds at equilibrium should depend only upon the condition of the surface regardless of its water content. Further, since the LVO compounds of interest are mostly insoluble, such compounds adsorbed on the surface will remain there. This can lead to considerable coverage of the surface by the adsorbed compounds and eventual formation of multiple layers. Choosing a theoretical description for this adsorption process

requires a formalism that can at least treat multiple layer formation for the LVO compounds. Such simple theoretical adsorption forms as Henry's Law assume small surface coverage of less than a monolayer, such as that occurring when the adsorbing compound is quickly adsorbed into the aerosol volume. Indeed, Henry's Law is often used in the limit of zero surface coverage. Realizing this, Junge (1977) adapted the theory of adsorption of gases (BET theory) proposed by Brunauer et al (1938) to estimate the relative aerosol/gas phase distribution due to adsorption of volatile organics in atmospheric aerosol. His treatment was general, and dependent upon assumptions about the binding energies and concentrations of vapor on the surface of the aerosol that were open to questions. However, application of his estimates by Hahn (1980) to the data of Eichmann et al (1979) was close enough to show that the BET theory held promise in providing estimates of LVO phase distributions.

Based on the validity of the theory and the preliminary results by Junge, the BET theory was chosen as the correct approach to the problem of estimating the aerosol/gas phase distribution for LVO in the atmosphere. In developing an estimator from the theory, an effort was made to carefully calculate each of the parameters called for by the theory. From the BET theory, the formalism describing multilayer adsorption of an LVO on atmospheric surfaces can be summarized by

$$\frac{v}{v_m} = \frac{cP}{(P_o - P)[1 + (c - 1)\, P/P_o]} = \frac{a}{a_m} \qquad (1)$$

where

$$c = \exp \frac{E_m - E_L}{RT}$$

Here

v = the volume of gas adsorbed on the aerosol surface

v_m = the volume of gas for a single adsorbed monolayer

P_o = the saturation vapor pressure of the volatile organic

P = the vapor pressure of the volatile organic

a = the concentration of the volatile organic on the aerosol surface (gm/cm^2)

a_m = the concentration of vapor on the surface for a complete monolayer (gm/cm^2)

E_m = the heat of adsorption of the first monolayer

E_L = the heat of liquefaction of the volatile organic

R and T are, respectively, the gas constant and ambient temperature in degrees K.

If S_a is the surface area concentration of ambient aerosol ($\mu m^2/cm^3$), the concentration of gas adsorbed on the aerosol surface is

$$m = S_a \times a \ (gm/cm^3) \ . \tag{2}$$

Also,

$$\rho = MP/RT \tag{3}$$

is the concentration of vapor in the gas phase. Here, M is the molecular weight of the volatile compound.

Combining Equations (1), (2), and (3), we can define the ratio of the organic concentration in aerosol to that in the gas phase as

$$\frac{m}{\rho} = \frac{ca_m S_a RT}{(P_o - P)[1 + (c-1)P/P_o]M} \tag{4}$$

In considering conditions in the atmosphere where equilibrium exists between gas and aerosol phases, two approximations can be made. First, $P \ll P_o$ is usually the case except for fresh emissions from an uncontrolled source. Second, the product cP is also small compared with P_o. Applying these approximations, Equation (4) becomes:

$$\frac{m}{\rho} = \frac{c\, a_m S_a RT}{P_o M}$$

We can now calculate the fraction of a volatile compound in the aerosol phase. This is just

$$f_a = \frac{m}{\rho + m} = \frac{c\, a_m S_a RT}{MP_o + c\, a_m S_a RT} \qquad (5)$$

This fraction is a strong function of ambient temperature (T) and available aerosol surface (S_a). The ambient temperature is determined by the season, and the available aerosol surface is a function of the locale, e.g. urban, rural, etc.

B. Phase Distribution of n-Alkanes in the Atmosphere

In applying the BET theory estimator for the fraction n-Alkane in ambient aerosol, a basic assumption was made about the nature of the surface involved: for the first monolayer, the surface behaved essentially like elemental carbon. This is justified since, apart from fresh combustion aerosol which is likely to be carbon, the aerosol surface is expected to act like a solid and be composed of organic or carbon components. If this assumption is not made, e.g. the surface is taken as water, the values obtained for E_m are significantly different and lead to very different values of f_a for high molecular weight Alkanes.

Values of parameters used in the estimator for the n-Alkanes were derived from the literature. a_m, the surface density of a monolayer was obtained from McClellan and Harnsberger (1967). This parameter had an asymtotic value of 3.10×10^{-8} g/cm^2. Saturation vapor pressure (P_o) was derived using the Tables of Schlessinger (1972). The heat of adsorption for a monolayer (E_m) and the heat of liquefaction (E_L) for the n-Alkanes on carbon was obtained using the data of Schaeffer, et al (1949) for Spheron 6. This is an aerosolized channel black manufactured

by Godfrey L. Cabot, Inc. Although indications are that this carbon black can differ in a specific area from other forms of carbon black, e.g. furnace carbon black, the methodology used by Sheaffer to deposit Spheron 6 produces a sample with specific surface comparable to furnace carbon black. Both these forms of carbon aerosol exhibit specific surface areas comparable to atmospheric aerosol, i.e. between 10 and 120 m^2/g. Other types of carbon may not exhibit the same adsorption characteristics unless they at least have a similar specific surface. Such forms of carbon were not investigated. Values for E_m and E_L were derived from BET adsorption isotherms for n-Alkane adsorption on the Spheron 6 at temperatures of 0 to 100°C. Since both E_m and E_L are linear as a function of the n-Alkane carbon number, c is given by:

$$c = \exp \; (1270 + 150\,N)/_{RT}$$

Here N is the carbon number of the n-Alkane and R is the gas constant in cal/mole °K. The calculation for phase distribution of the n-Alkanes was made for three aerosol concentrations representative of urban, rural and remote sampling sites (Whitby and Cantrell, 1976). Three average seasonal ambient temperatures were also used representative of summer, autumn, spring, and winter. Values used for aerosol surface and temperature are shown in the following table.

Table 1

PARAMETERS USED IN ESTIMATOR

Locale	Aerosol Surface $\mu m^2/cm^3$	Season	Average Temperature ^oK
Urban	1000	Summer	300
Rural	200	Autumn/Spring	290
Remote	30	Winter	275

Before using P_o in Equation (5) it was corrected for aerosol surface curvature effects using the Kelvin correction. This vapor pressure correction referenced to aerosol diameter d_p is described in Adamson (1982), and can be expressed as

$$P_p = P_o e^{-\frac{4\sigma \bar{v}}{RTd_p}}$$

Here

σ = the surface tension of the aerosol
$\bar{v}$ = the molar volume of the surface material
d_p = the diameter of the aerosol.

This correction is relatively small for aerosol in the accumulation mode (d_p ~ = 0.2 μm). The correction for typical atmospheric aerosol was approximately 16 percent for n-octacosane. Values of the fraction of volatile compound in the aerosol phase for the n-Alkanes are tabulated in the Appendix for each season and locale given in Table 1.

Results of the BET theory estimation of the aerosol/gas phase distribution for summer, i.e. n-Alkane concentrations showing the effect of varying ambient aerosol surface concentration, are shown in Figure 1. As aerosol surface concentration decreases, so does the fraction of n-Alkane found in the aerosol. In any event, the amount of n-Alkane found in ambient aerosol is negligible for carbon numbers less than 18. The effect of seasonal temperature changes for an urban aerosol are depicted in Figure 2. As average seasonal temperatures decrease, more of the organic material is found in the aerosol. However, n-Alkanes with carbon number less than 18 are still mostly gas phase; less than 10 percent are in the aerosol phase. Figure 3 compares the data of Broddin et al (1980), with the BET calculation for a summer-urban n-Alkane phase distribution. Figure 4 compares the data of Van Vaeck et al (1984), with the BET calculation for an autumn-rural n-Alkane phase distribution. Figure 5 compares the data of both Broddin et al and Van Vaeck

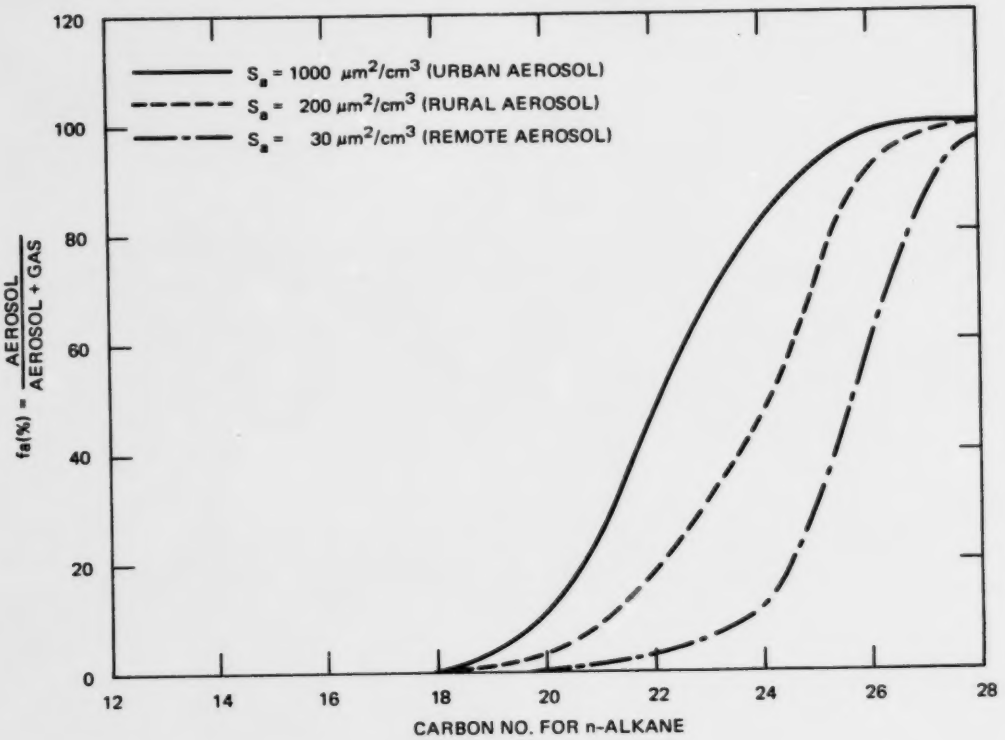

FIGURE 1 FRACTION OF n-ALKANES IN THE AEROSOL PHASE CALCULATED FROM THE BET THEORY AS A FUNCTION OF LOCALE FOR A TYPICAL AVERAGE SUMMER TEMPERATURE; T = 300°K

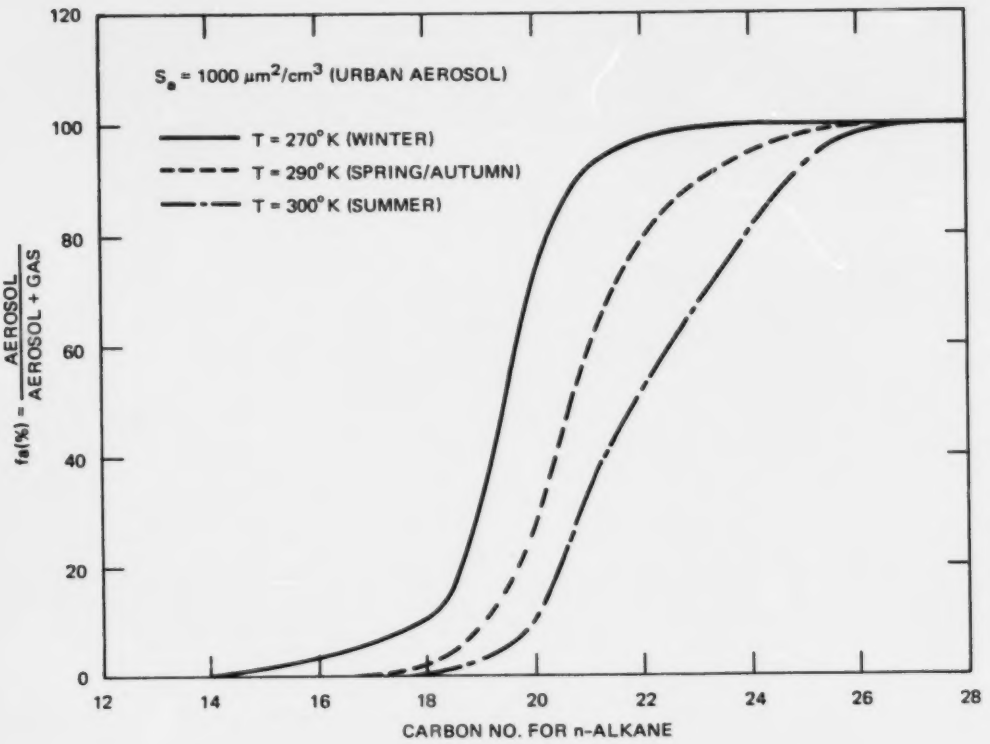

FIGURE 2 FRACTION OF n-ALKANES IN THE AEROSOL PHASE CALCULATED FROM THE BET THEORY AS A FUNCTION OF SEASON FOR A TYPICAL URBAN AEROSOL SURFACE CONCENTRATION

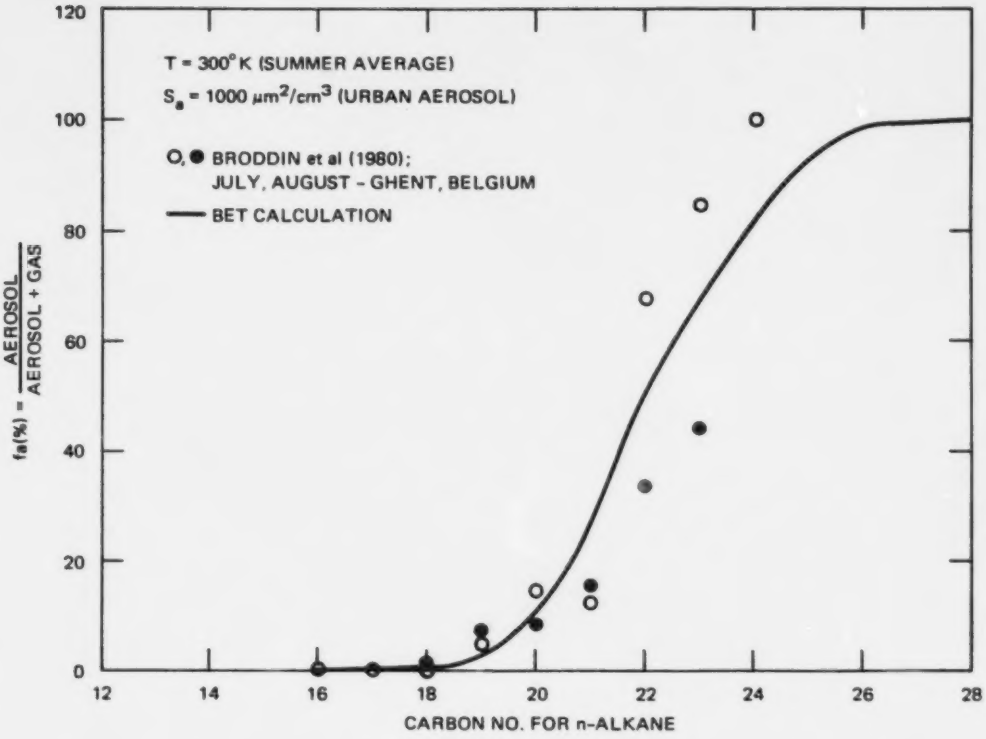

FIGURE 3 COMPARISON OF THE FRACTION OF n-ALKANE IN THE AEROSOL PHASE, MEASURED BY BRODDIN ET AL (1980) WITH PHASE DISTRIBUTION PREDICTED FROM THE BET THEORY

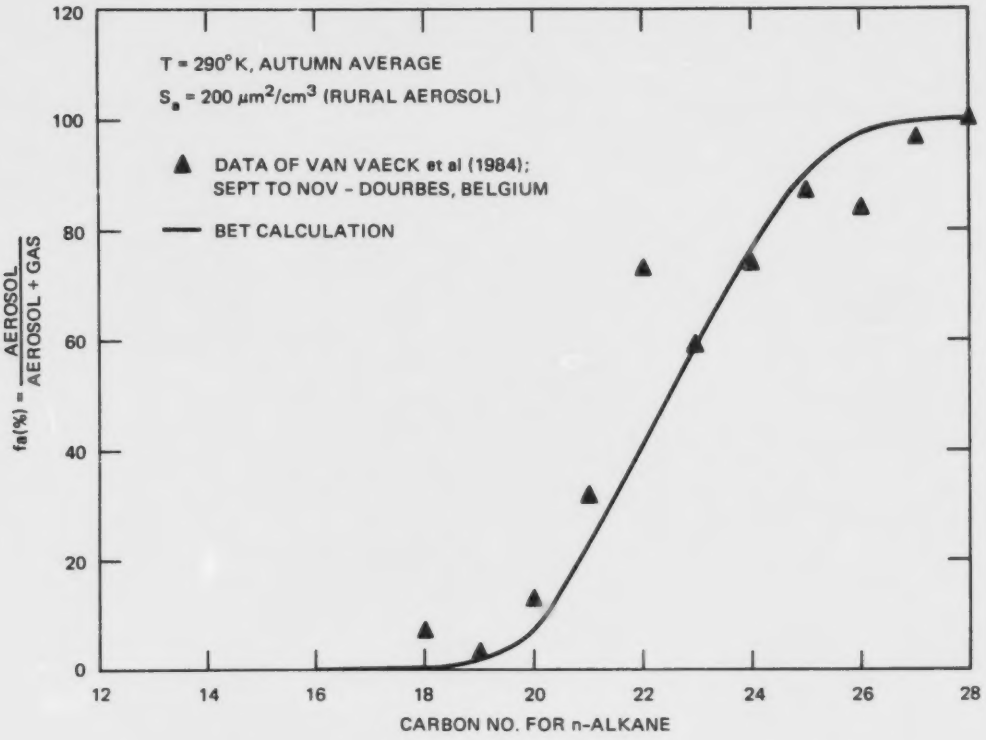

FIGURE 4 COMPARISON OF THE FRACTION OF n-ALKANE IN THE AEROSOL PHASE, AS MEASURED BY VAN VAECK ET AL (1984) WITH PHASE DISTRIBUTION PREDICTED FROM THE BET THEORY FOR AN AUTUMN/ RURAL AEROSOL

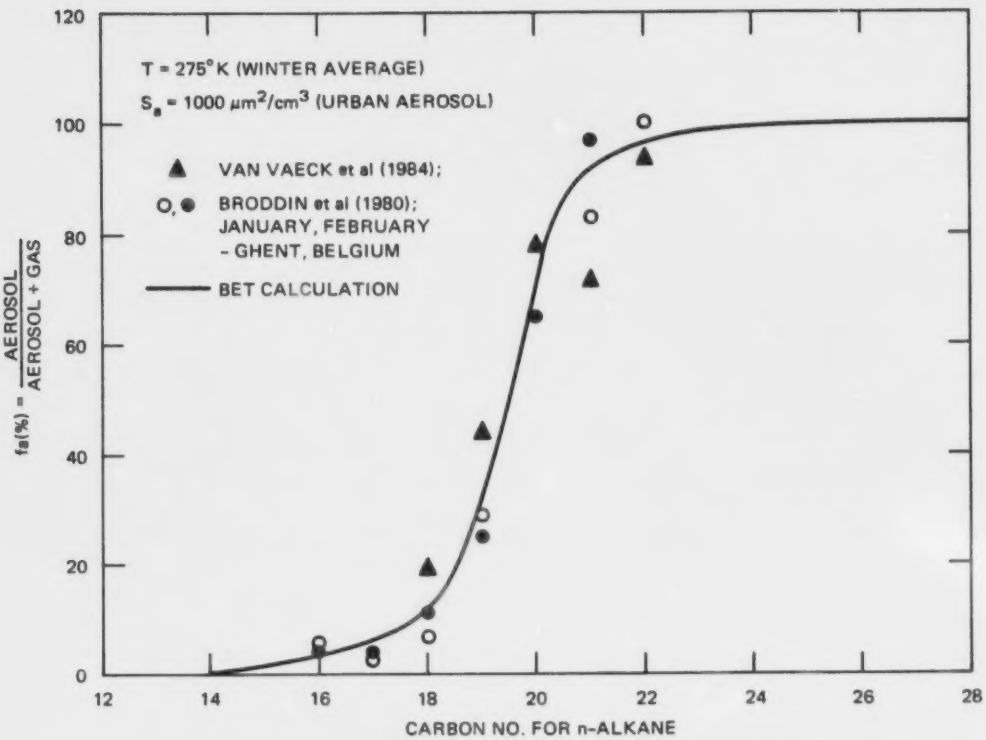

FIGURE 5 COMPARISON OF THE FRACTION OF n-ALKANE IN THE AEROSOL PHASE, AS MEASURED BY VAN VAECK ET AL (1984) AND BRODDIN ET AL (1980) WITH THE PHASE DISTRIBUTION PREDICTED FROM THE BET THEORY FOR WINTER/URBAN AEROSOL

et al with the BET calculation for a winter-urban n-Alkane phase distribution. Each of these comparisons are with data where some attempt has been made to minimize or correct for sampling loss and artifact formation. As pointed out in Section II, data for which this has not been done cannot be trusted. Comparisons of the BET calculation with the data is probably within experimental error. However, since neither experimental error, average temperatures nor ambient aerosol surface concentrations are given in the papers quoted, an exact statistical comparison cannot be made with the available experimental data.

C. BET Estimator Limitations

There are two basic limitations to the BET calculation. These are the availability of the adsorption parameters E_1, E_L, and a_m; and, if comparison is to be made with field measurements, concurrent information on ambient temperature and aerosol surface concentrations. Since the n-Alkanes are a family of compounds that have been extensively investigated over the past 40 years, enough information is available on the adsorption parameters to make a creditable attempt to calculate aerosol/gas phase distributions. The necessary temperature and aerosol surface concentration data are simply a matter of incorporating these measurements into the experimental protocol. Another limitation for the calculation is the reliability of the values obtained for the saturation vapor pressure of high molecular weight compounds. It is possible that the value of P_o used for Docosane is in error by as much as a factor of two. The net effect in the calculation for the n-Alkanes is slight; but a similar uncertainty for another type of compound could cause an error in the phase distribution calculation of almost 40 percent. Although not used in this work, selected values of physical and thermodynamic properties of LVO hydrocarbons and related compounds are available in publications of the American Petroleum Institute Project No. 44 (1953).

This reference does not contain information on PAHs. Some data for the latter is given by Mackay and Shiu (1981).

We have not treated other types of special aerosol surfaces known to exist in the atmosphere, e.g. sea salt, soil dust, fly ash etc., because of a lack of information in the literature on the adsorption properties of LVO on such surfaces. These aerosol are only important individually near their sources. In such special cases, specific experiments would need to be performed to obtain the necessary adsorption parameters for a specific LVO and the special aerosol surfaces involved. An aged continental aerosol would probably be a mixed aerosol with quite different surface characteristics. The data of Van Vaeck et al. (1984) that was compared in Figures 1 through 5 with the BET estimate of phase distribution is for such aged atmospheric aerosol. The success of the BET formalism in estimating these average atmospheric phase distributions for the n-Alkanes, using the simplifying assumption of a carbon type aerosol, may indicate that such an aged atmospheric aerosol has similar adsorption properties; therefore, one need not consider the separate components from which the atmospheric aerosol is composed. This similarity in surface behavior with regard to absorption of LVO compounds is a subject which requires further study.

As pointed out above, only the n-Alkanes have been treated in this work because little information is available in the literature on surface adsorption of other LVO compounds measured in the atmosphere. To derive estimates of the appropriate adsorption parameters from first principles would require application of statistical mechanical considerations similar to those used by Hill (1956). In developing such estimates, it would be necessary to first select the theoretical models to be used, and then conclusively define the characteristics of the aerosol surfaces to be considered. Models for such gas-solid adsorption isotherms have been reviewed by Cortes (1985). These considerations are beyond the scope of this investigation, but indicate a direction for future efforts on the problem.

With respect to the effect of the solubility of an LVO in water, the effect is negligible if our assumption about the surface characteristics of atmospheric aerosol is correct, and the LVO is relatively insoluble. If the LVO is relatively soluble, then different values of E_1 and E_L should be used. These can be obtained from BET adsorption isotherms of the compound on water. For example, the work of Dorris and Gray (1981a,b) would provide useful data for n-Alkanes if solubility were a factor with atmospheric aerosol. If the compound is highly soluble, a different estimator based on Henry's constant should be used. Such a scheme was proposed by Heicklen (1981). It depends directly upon the solubility of the compound in water to calculate the relative aerosol/gas distribution.

D. Considerations Near an Alkane Source

Two types of n-Alkane sources usually exist in urban areas. These are the uncontrolled direct sources that emit saturated vapor and aerosol, and the more common controlled type that emits unsaturated vapor only.

Modification of the BET Estimator for Uncontrolled LVO Sources - For LVO in the plume of an uncontrolled source, the two simplifying assumptions made in the section on the BET estimator are no longer valid. Equation (5) then becomes:

$$f_a = \frac{c a_m S_a RT}{(P_o - P)\,[1 + (c-1)\,P/P_o]\,M + c\,a_m S_a RT} \qquad (6)$$

Here $$P = \rho RT/M.$$

As can be seen, the estimator is not usable until the value of P falls below P_o. From that point, f_a decreases until it reaches the equilibrium value given by Equation (5). In most emission plumes this process

is very rapid. Because of this, Equation (6) will have a very limited use in predicting LVO phase distributions. For that portion of the plume where the LVO vapor is saturated, a non equilibrium situation exists: the aerosol surface is growing rapidly, some LVO aerosol may be lost to deposition, and rapid dilution and cooling is occurring. Such a dynamic process requires a completely different theoretical description. If the LVO loss is minimal during this period, it is not necessary to consider the LVO phase distribution since conditions in this portion of the plume are so transient. Estimation of aerosol loss to deposition during this period would require that a plume model be accurate over the first few minutes of plume life. Beyond this, equilibrium conditions are quickly approached, and phase distribution determinations should be amenable to the BET estimator given in Equation (5).

Controlled Source - A controlled source of n-Alkane usually employs a device similar to the SMOG-HOG of United Air Specialists, Inc. This device processes the effluent by cooling the vapor, and then precipitating the resultant aerosol with an ESP. This cycle can be repeated several times before the vapor is discharged into the atmosphere. The result is the discharge of an unsaturated vapor that should quickly reach equilibrium with ambient aerosol concentrations. Such a condition should readily be describable using the BET formalism of Equation (5).

A similar situation exists when LVO is released from a storage facility such as a holding pond. Again, equilibrium with atmospheric aerosol concentrations should be almost immediate, and the phase distribution should be calculable using the BET estimation protocol.

IV SRI SAMPLING PROTOCOL FOR LVO

A. Introduction

The traditional sampling protocol used when aerosol/vapor phase distributions are required, as discussed in Section II, is a high-volume filter sampler, followed by a vapor trap. This arrangement, shown in Figure 6, has serious problems--particularly when sampling periods extend to 24 hours and beyond. The principal physical problem is loss of organic aerosol material from the filter as vapor, and subsequent collection of this by the vapor trap. This yields an incorrect partition between aerosol and vapor which can invalidate the results of such collections.

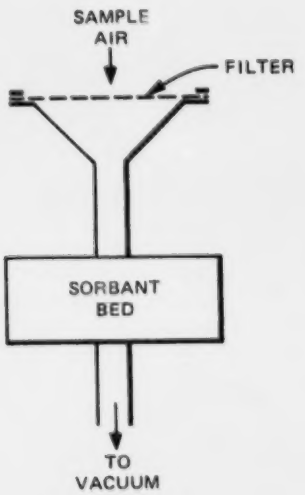

FIGURE 6 BLOCK DIAGRAM OF "TRADITIONAL" SAMPLING TRAIN FOR PHASE SELECTIVE SAMPLING OF ORGANIC POLLUTANTS

Such losses were determined quantitatively for the n-Alkanes by Van Vaeck et al (1984). Peters and Seifert (1980) found that for benzo(a)-pyrene, dark losses can also be 50 percent, and under extremes of heat

were as much as 90 percent. In other work, Konig et al (1980), found losses of 78 percent when working with fluoranthene. This was improved to a 13 percent loss by impregnating the filter with a resin absorbent. However, in an atmospheric sampling situation the question also arises as to how much of the vapor is also trapped on such a filter, resulting in a phase partition biased towards the aerosol.

Another problem is that which is associated with reactions between the filter media and collected aerosol; an example of such a reaction is neutralization of acids by basic media which yields a salt that may not be recoverable by the analysis procedures. Chemical degradation of a sample can also occur from reactions between atmospheric gases found in polluted urban air and the collected sample. This is particularly true for protracted sampling periods, when large amounts of sample air are drawn past material collected on that filter. Reactions with atmospheric gases, e.g. nitration of collected material with NO_x or oxidation by ozone, constitute a major failing of the traditional sampling method, in fact, of any technique where collected material is exposed to subsequently sampled air.

SRI has attempted to develop a sampling protocol that addresses the major physical drawbacks of the "traditional" method. The sampling device used, shown schematically in Figure 7, is a train of at least four consecutive components through which sample air is drawn. The first component is a size selective inlet with a 10 μm cut size; the second is a "denuder", which removes and traps the organic vapor phase component of the sample. The next component is a filter to collect the aerosol portion of the sample stream. Finally, a vapor trap collects the organic vapor from the stream which results from volatilization of the filter-collected aerosol. The aerosol fraction of the sample is the sum of the material collected on the filter and the final trap. The denuder was designed to be thermally desorbed, and a direct measure of the vapor fraction obtained.

The SRI sampling protocol has none of the major physical drawbacks of the more traditional method. The problem of filter media interaction

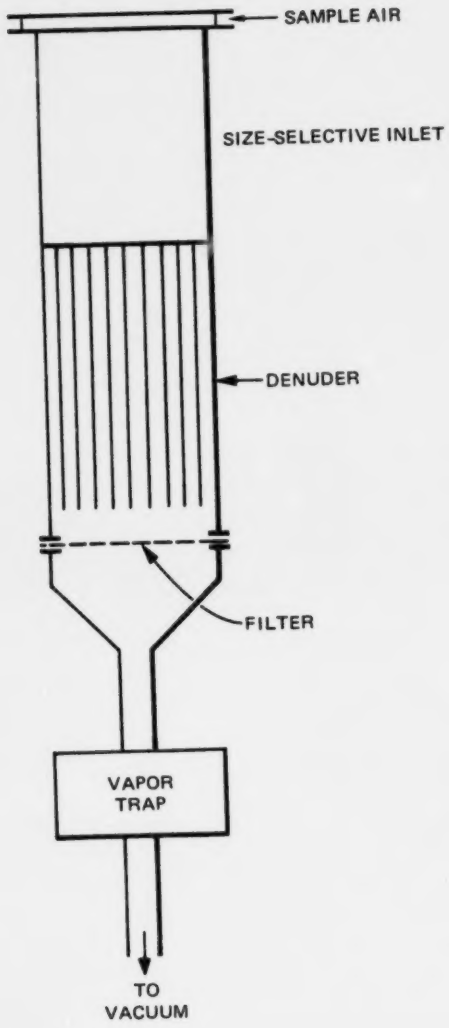

FIGURE 7 BLOCK DIAGRAM OF "DENUDER" SAMPLING TRAIN FOR PHASE SELECTIVE SAMPLING OF ORGANIC POLLUTANTS

that remains can be minimized by a proper choice of media. Reaction of the collected sample with other atmospheric gases can be minimized by using the procedures of Van Vaeck et al (1984) as discussed in Section II of this report.

B. Sampler Design

Design of the SRI sampling train was in two parts: the design of the 10 μm size selective inlet, and the design of the denuder assembly to remove the LVO vapor while passing atmospheric aerosol to the filter element. The sampler is depicted in the assembly drawing of Figure 8. Except for choice of filter and the specific use protocol, the filter and post aerosol sample trap are expected to be of a type used in previous sampling attempts by Broddin et al (1980) and Van Vaeck et al (1984).

Inlet Design - Sampler inlet design is based on the approach of Liu and Pui (1981) in designing aerosol sampling inlets for inhalable particles. The impactor, pictured in Figure 9, draws the sample through a circular slot defined by the circular sampler cover and the impactor body top. The sample then passes through a funnel to the impactor nozzle. The impactor is formed by a cup placed under the nozzle. Sample air then passes through a 6 inch diameter x 24 inch duct to the denuder assembly. A sample flow of 100 lpm was chosen because this yields an adequate sample of the LVO of interest, assuming that the urban concentrations of Van Vaeck et al are correct. For the sample flow of 100 lpm, a 50 percent efficiency is achieved by the impactor at 10 μm particle diameter (D_{p50}=10 μm) for a jet diameter (W) to impaction surface spacing (S) ratio of S/W = 0.95. Actual dimensions are indicated in the figure.

Denuder Design - The basic denuder configuration chosen for this study is an assembly of parallel, laminar flow tubes. Laminar flow in the tubes is preferred because the percent of vapor or particles removed

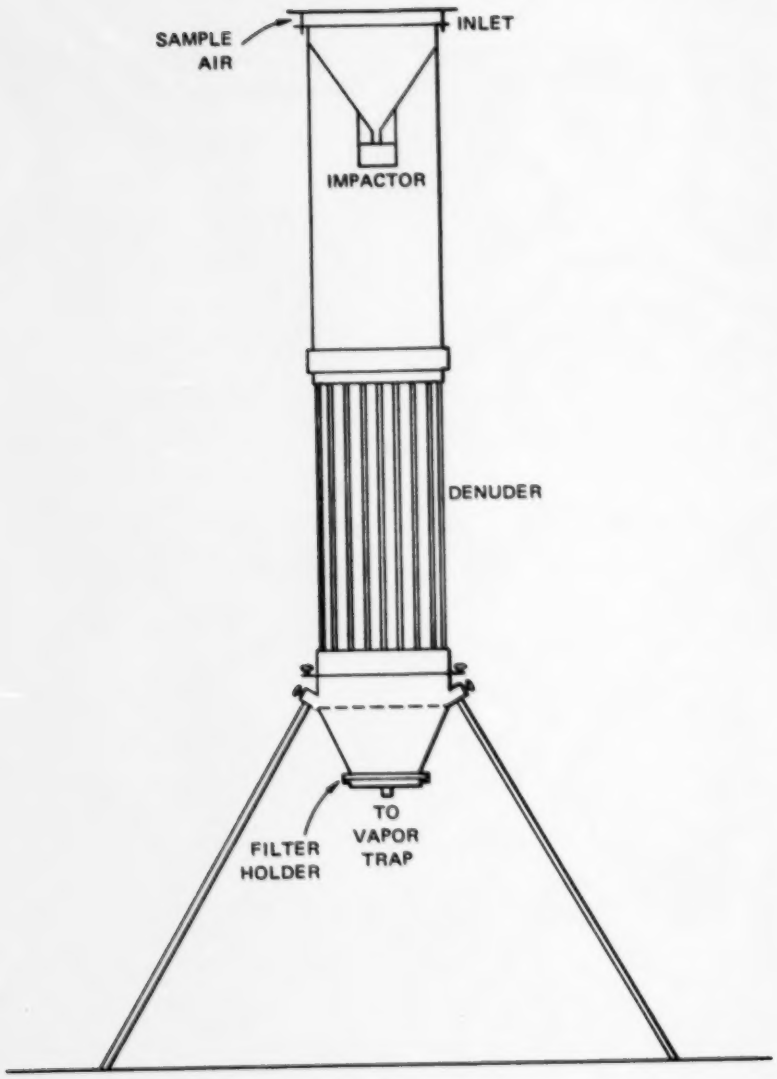

FIGURE 8 DENUDER-SAMPLER ASSEMBLY DRAWING

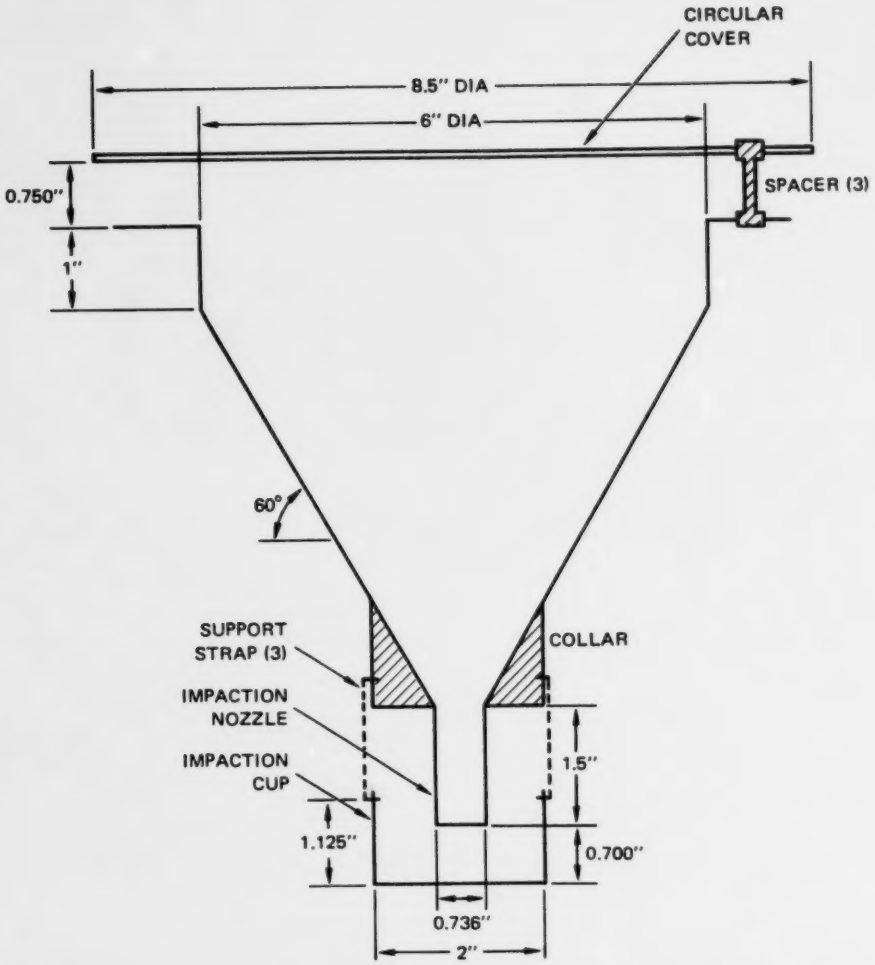

FIGURE 9 SAMPLER IMPACTOR INLET

is exponentially dependent upon the diffusion coefficient (D) and, hence, operates quickly. The differential action of the denuder on gases as opposed to aerosols depends on the differences in their diffusion rates. This result allows for efficient vapor/particle separation. A multiple tube design gives the least obstruction to aerosol passage, and optimum vapor adsorption. The specific design approach used was that of Gormley and Kennedy (1949). Their equation to estimate the loss of each component of the sample vapor and aerosol to the wall of the denuder tubes by diffusion is given in the following. For a given component of the sample flow the concentration C at the end of a tube is:

$$C = C_0 [0.819 \exp(-3.657\,\alpha) + 0.097 \exp(-22.3\,\alpha) + 0.33 \exp(-57\,\alpha)]. \quad (7)$$

Here,

Sample flow in the tubes was laminar with Reynolds number of 100.

C_o = the concentration entering the tube

$\alpha = \pi DL/Q$

D = the diffusion coefficient of the component

L = the length of the tube

Q = the volume flow rate.

The equation for the diffusion coefficient of the vapor component D_{vapor} is derived from Bird et al (1960) with the basic assumption that air is the carrier gas:

$$D_{vapor} = 7.089 \times 10^{-5} \sqrt{\frac{T^{1.5}(1/M_a + 1/M)}{P}}$$

Here,

T = the temperature in degrees Kelvin
M_a = the molecular weight of air
M = the molecular weight of the vapor species
P = the pressure.

The diffusion coefficient of the aerosol is

$$D_a = KTS/3 \pi \eta D_p .$$

Here,

K = the Boltzman constant
T = the temperature in degrees Kelvin
S = the slip correction factor
η = the viscosity of the air
D_p = the diameter of the aerosol.

To determine the number, diameter, and the length of tubes the following sampling criteria were used:

Sample Flow Rate = 100 lpm
Vapor retention $\geq$ 98 percent
Aerosol transmission for 0.1 μm aerosol > 99.5 percent
Sampling temperature = 298° Kelvin
Pressure = one atmosphere.

Given these criteria, the number of tubes used was 163, length was 60 cm, and diameter was 0.5 cm. The material chosen for the denuder body was stainless steel. This provides adequate thermal conductivity when the denuder is thermally desorbed, and an inert substrate for the adsorbing lining of the tube.

Tube Coating - The denuder design procedure used in the preceding section assumes that the walls of the tubes are one-hundred percent efficient in adsorbing LVO vapor. As pointed out in Section II, this depends on the adsorber and the particular LVO vapor being adsorbed. Tenax was chosen as the adsorber of choice because it could readily be attached to the tube walls, could be thermally desorbed, and would operate over a wide range of relative humidities. This particular adsorbent has a decreasing desorption efficiency for n-Alkanes with a carbon number greater than 16. However, because the adhesive necessary to attach the Tenax to the inside of the denuder tubes also has adsorbent properties, the combined adsorbent/adhesive system must be evaluated for its net adsorption/desorption characteristics.

Aerosol Sample Collection - As designed, the denuder will perturb the aerosol system that it samples. Since the denuder will remove all LVO vapor from the sample, it will initiate desorption of these compounds from the aerosol surface. This will eventually remove the more volatile components from the aerosol. This process, however, takes more time to effectively remove LVO from the aerosol that its 1 sec. residence in the denuder will permit. Hence, the denuder should remove all LVO from the sample air without seriously perturbing the aerosol fraction.

The aerosol will then be deposited on the afterfilter where it will be exposed to LVO free air over a considerable time period, up to 12 hours. It is at this point that desorption loss of LVO from the collected aerosol is expected to take place. Such lost sample material can be recovered using a post filter vapor trap which will remove all LVO compounds from the sample air. This sample would be analyzed and the result combined with that of the afterfilter to obtain the total aerosol associated LVO concentration.

Two considerations govern the choice of filter media to be used. First, the filter media must not change the character of the particulate collected or interfere with the analysis. Second, the media must have a low pressure-drop characteristic for the sampling flow rates used and

still provide efficient filtration for submicron aerosols. This second requirement is to prevent the loss of heavy organic vapors from the particulate during the sampling process. The media that meets both these requirements is the Giha 2-μm laminate Teflon filter (Giha Corporation, Pleasanton, California). It has a pressure drop of only 1 cm Hg for nominal rates of 0.1 m^3/min through a 100-mm disk filter, and yet has an aerosol penetration of less than 1 percent at 0.3 μm.

C. Sampler Component Evaluation

To obtain operating characteristics, the principal components of the SRI sampler--the inlet impactor and denuder assembly--were evaluated separately for aerosol transmission. The denuder was evaluated for LVO adsorption efficiency and breakthrough using an n-Alkane standard on single tubes. This latter was done to speed denuder evaluation, and to facilitate testing of different adsorbents. The entire assembly was then evaluated using the same n-Alkane LVO standard in ambient air.

Inlet Performance - The inlet impactor was tested in the SRI aerosol test facility using non-volatile ammonium fluorescein aerosol. The aerosol was generated using a sonic nebulizer which produces a monodisperse aerosol of known size. Since this impactor design has already been evaluated by Liu and Pui, only two test aerosol sizes were generated, 1.0 and 10 μm. The aerosol collected by the impactor and an after-filter is washed from the impactor cup and filter media, and analyzed using a fluorometer. A comparison of the results of these measurements with the theoretical collection efficiency curve is given in Figure 10. As can be seen, the measured value of 51 percent for a 10 μm test aerosol for the rated flow of 10 μm agrees with the design value of D_{p50} = 10 μm. Measured loss of aerosol to the funnel is less than 1.5 percent.

Denuder Aerosol Transmission Tests - Aerosol transmission through the denuder was measured using the same test facility and aerosol

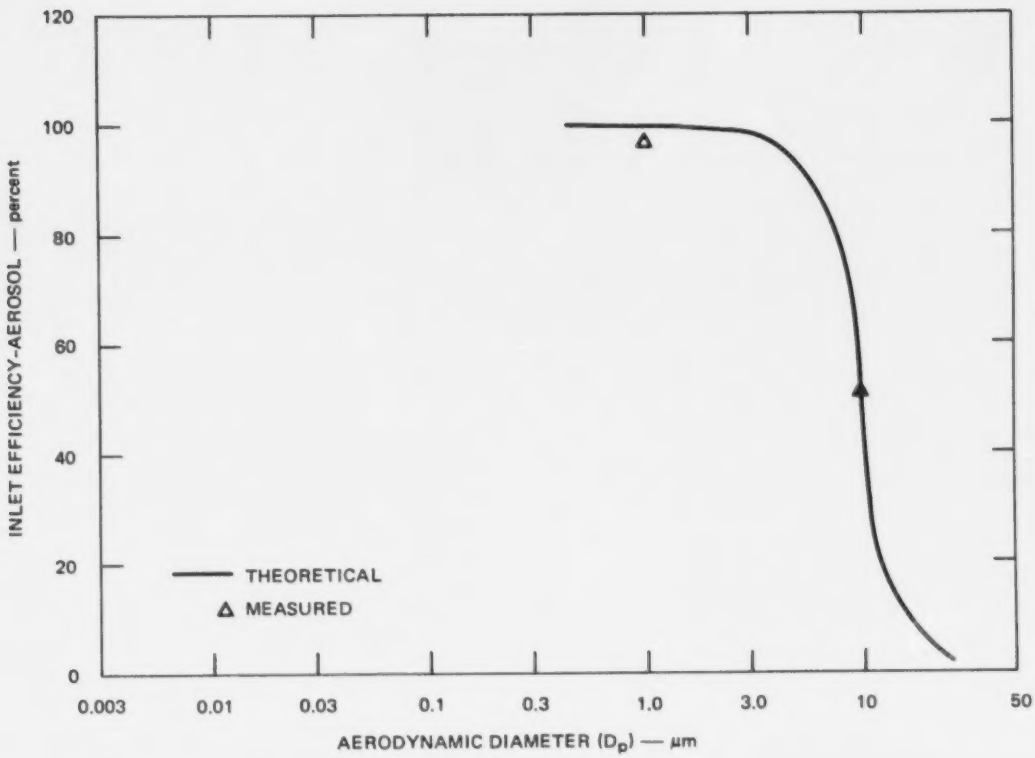

FIGURE 10 COMPARISON OF MEASURED INLET IMPACTOR COLLECTION EFFICIENCY WITH THEORY OF LIU AND PUI (1979)

generating equipment as that used in evaluating the inlet impactor. Figure 11 presents the results of these tests for the rated sample flow. As can be seen, the aerosol loss is less than 2 percent for aerosol from 0.2 to 10 μm diameter in size. The slight decrease in efficiency near 10 μm is accounted for by impaction with the front face of the denuder assembly. For these measurements, the denuder tubes were bare. Since the Tenax bead size chosen--2 μm diameter--is less than the boundary layer thickness in the tube during sampling, the beads should not have any effect on aerosol loss in the tubes.

Quality assurance procedures used in evaluating the denuder were as follows:

- Laminar flow in the test facility manifold was achieved using the extended length (6') of 6" ducting before the denuder in the manifold.
- Aerosol was generated using a sonic nebulizer. Size and concentration of the aerosol was determined with a multi-stage impactor using piezo-electric substrates. These measurements were validated using optical microscope particle-counting techniques.
- Sample flow rate through the denuder was set using a critical orifice. Assurance for flow was obtained using a Kurz mass flowmeter in series, which is then traceable to NBS standard test No. 213-31/1905-22.
- The fluorometer measurements for deposited fluorescein aerosol are backed by standards prepared in-house. Results of these measurements are, in turn, cross-checked using the aerosol mass balance derived from piezo-electric balance measurements upstream and downstream from the denuder.

Single Tube Denuder Tests - Single tubes were acquired and prepared to evaluate adsorption from the gas phase of the compounds of interest. In this manner, we evaluated adsorption properties of several adsorbents, and included the use of controls in the experiment. This would be impossible using the entire denuder assembly. Once an adsorbent was selected, a final test using the entire denuder was made. This provided only the final validation of the completed denuder.

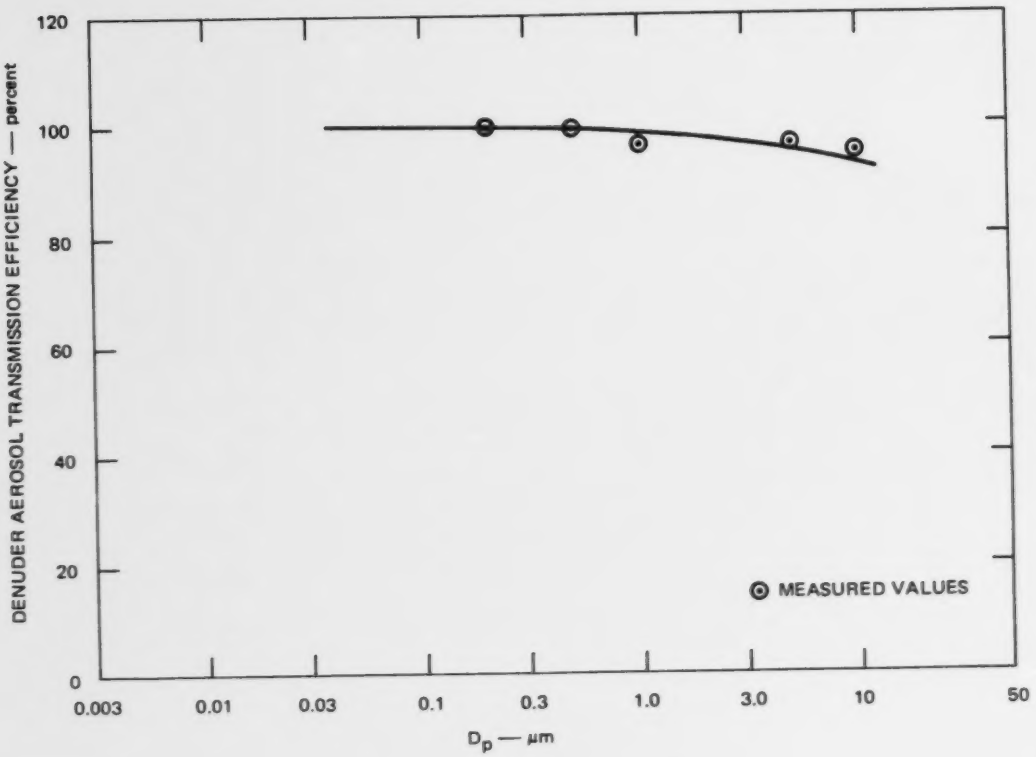

FIGURE 11 AEROSOL TRANSMISSION EXPRESSED AS PERCENT THROUGH THE DENUDER ASSEMBLY AS A FUNCTION OF AEROSOL DIAMETER

Initial protocol for adsorbent evaluation included the following configurations for coating the inside tube surface:

(1) Control -- bare tube
(2) 2 μm Tenax on a ceramic adhesive coating
(3) SE-30 on bare tube surface
(4) SE-30 on a ceramic adhesive coating
(5) Ceramic adhesive coating.

The last configuration was used to assess the relative effect of the ceramic adhesive and bare tubing. The ceramic adhesive coating used were Dow/Corning RTV643 junction coating and RTV3140 aluminum adhesive. Both cure to a ceramic (inorganic) finish. A composite standard used during the evaluation included the n-Alkanes with carbon numbers 10 through 24.

Evaluation arrangements for denuder sections under test are shown in Figure 12. A test sample is injected by syringe through a heated tee packed with glass wool. The vaporized sample is passed from the tee in an induced air flow into the denuder section under test. The denuder section is operated at ambient temperature during this first collection phase. Sample air passes from the denuder to a cryogenic sample loop which collects any components of the sample passing through the denuder.

After a specific volume of air has been sampled, the sample loop is chromatographically analyzed using a 30 meter DB-5 capillary column. Figure 13 presents the resulting GC analysis trace obtained from desorbtion of a standard sample from a Tenax/ceramic tube. The denuder tube is desorbed at a temperature of 200°C. Sample loop release is achieved at greater than 200°C. The sample collected in the denuder tube was equivalent to a 12 hr. atmospheric sample with LVO concentrations of approximately 6 ppb. The actual sample injected was 100 ng each of n-decane ($C_{10}H_{22}$) through n-tetracosane ($C_{24}H_{50}$) in 10 μl of n-hexane. Results indicated that the use of SE-30 as an adsorbtive coating is not suitable for the purposes of this study. Evidence of sample

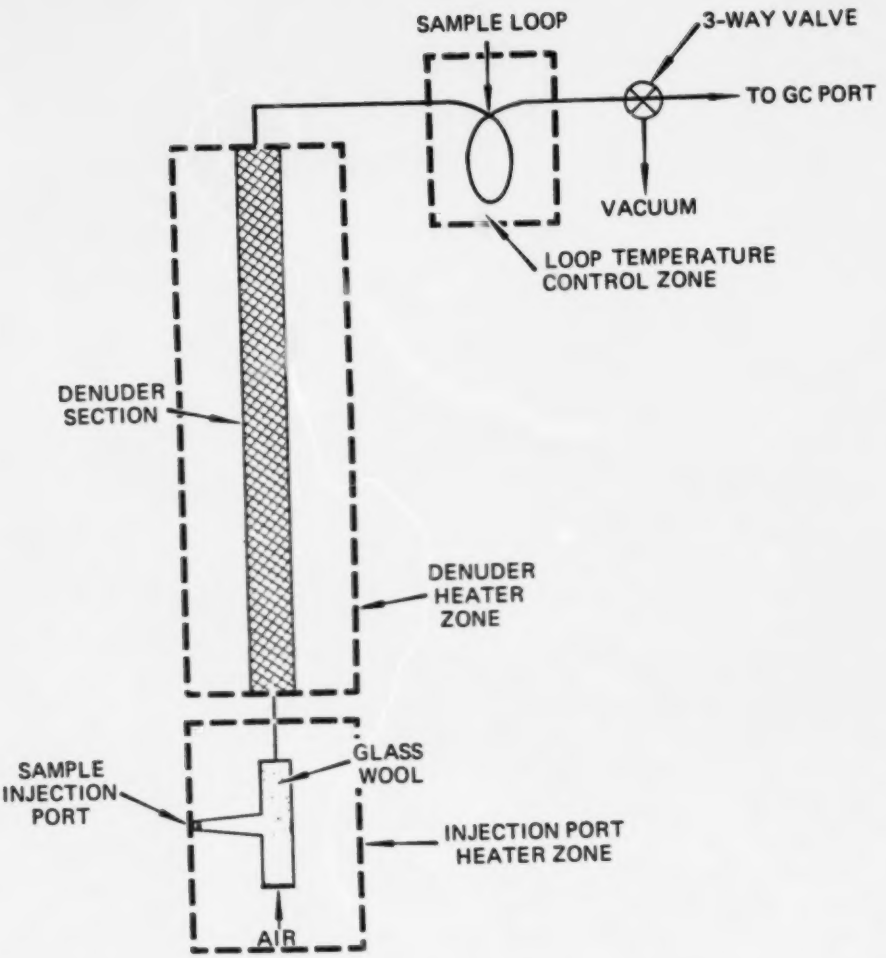

FIGURE 12 DENUDER SECTION EVALUATION AND TEST ASSEMBLY

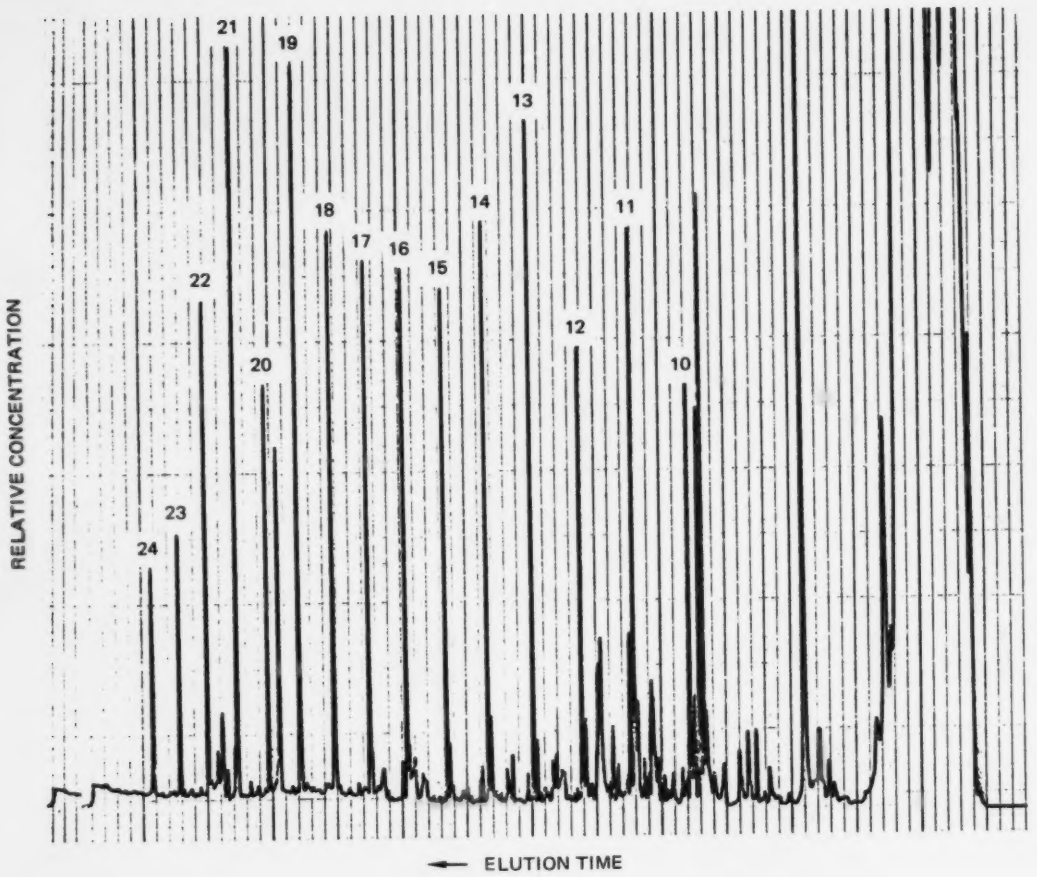

FIGURE 13 DESORPTION GC ANALYSIS TRACE OF SINGLE DENUDER TUBE COATED WITH TENAX/CERAMIC ADSORBER. CARBON NUMBERS OF STANDARD PEAKS ARE INDICATED ON FIGURE.

n-Alkane standard was used as a test LVO.

breakthrough for this coating was noted after a very small volume of sample air had passed through the denuder section under test. Test results for a Tenax-coated denuder tube indicated 100 percent adsorption efficiency with no indication of breakthrough for alkanes between n-decane and n-heptadecane. All tubes tested failed to retain hexane. Since denuder efficiency using Tenax was apparently adequate, the Tenax was selected as the adsorber of choice.

A final adhesive selection was made for the denuder section of the sampler: Dow-Corning RTV643 silicone junction coating. This adhesive has a usable temperature limit of 250°C, and will not collect water vapor. An unexpected plus is that the adhesive acts as an adsorber on its own, with an approximate 60 percent collection efficiency for n-alkane vapor with a carbon number of 16 or greater. Thus, the combination of Tenax and the Dow-Corning adhesive complement each other, and extend the range of action of the denuder from an alkane carbon number of 10 to 24. The combined recovery efficiency for a single denuder tube is plotted in Figure 14. The reduced recovery for Carbon number 22 and above can be ascribed to a reduced desorbtion temperature of 200°C. This was necessary to reduce background interference during analysis. An example of a desorption chromatogram showing n-Alkane atmospheric concentrations is given in Figure 15.

The denuder evaluation proceeded to the measurement of breakthrough volume for the denuder sections under test. Results of the tests indicate that a lower bound of 580 m^3 can be assigned to the breakthrough volume for a single denuder section. The measurement was done using four Tenax-coated sections of the denuder, each prepared in the same way. Each was spiked with an identical standard sample after being purged at 200°C with nitrogen for 24 hours. The denuder sections were then connected to a manifold, and 600 cm^3/min nitrogen was passed through each of the sections. The first denuder section was removed after one day, the second after two days, and so on. Each section was then desorbed and anlyzed. The results were compared with a previous standard sample run with the section before the test was started.

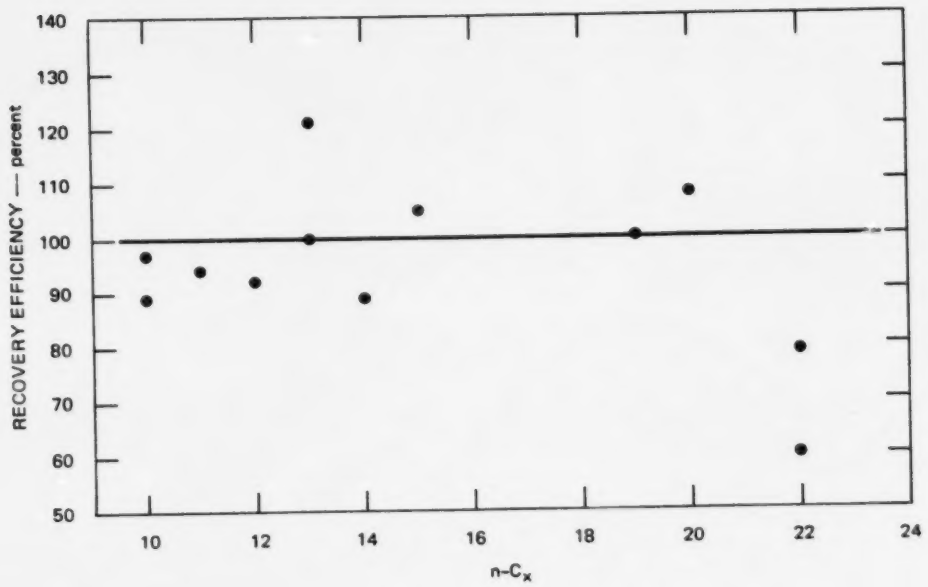

FIGURE 14 RECOVERY EFFICIENCY OF A SINGLE DENUDER TUBE

This represents the combined efficiency of tenax plus the Dow-Corning adhesive.

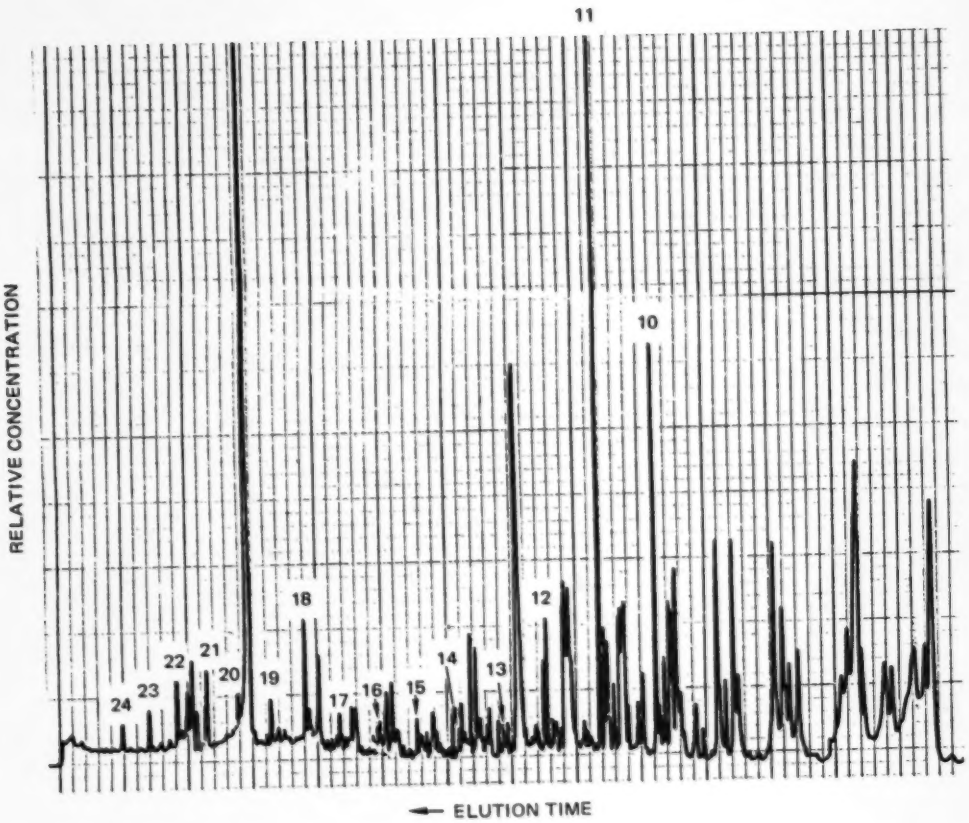

FIGURE 15 DESORPTION GC ANALYSIS TRACE OF SINGLE DENUDER TUBE COATED WITH TENAX/CERAMIC ADSORBER. CARBON NUMBERS OF ELUTES ARE INDICATED ON FIGURE.

Three hour ambient air sample.

Within the limits of repeatability of the denuder section, sample loss was then determined.

Preliminary specifications projected for the complete denuder assembly, based on the performance of the single tube sections can be summarized as follows:

Initial Vapor Collection Efficiency	100 percent for n-Alkanes, carbon number 10 through 24
Breakthrough Volume (reduction by 1/e)	8256 m^3
Thermal Desorption Recovery Efficiency for n-Alkanes	0.84 ± 0.14 percent for carbon number 10 through 20
Denuder Aerosol Transmission Efficiency	>99 percent for diameters < 1 µm
	>94 percent for diameters < 10 µm
Sample Flow	100 lpm
Filter Size	90 mm
Inlet Size Limit	10 µm, 50 percent transmission efficiency

The limit of a carbon number of 20 for the recovery efficiency of the n-Alkanes is the result of reducing the desorption temperature to reduce background interference during analysis.

Full Denuder Tests - The full sampling assembly with denuder is pictured in Figure 16. In addition to scaling the denuder up from one tube to 163, the desorption oven was also scaled up to acommodate the increased size. The oven and denuder are pictured with the gas chromatograph used for sample analysis, in Figure 17(a,b). After coating the denuder assembly with adhesive and Tenax-GC particles, the denuder was assembled and heat-cured at 225°C with constant nitrogen purge for 10 days. The purge gas was sampled and analyzed by GC without cooling the denuder or exposing it to air. The resulting chromatogram, Figure 18, showed the presence of interfering material, but at a low enough level so that standards could be recovered from the assembly.

In preparing the full denuder for sampling and analysis, the connection of the denuder to the transfer caps presented a substantial problem. The original gaskets used were made from a high temperature silicone rubber septum material. At the temperatures used to desorb the denuder (200°C), the gasket material "bleeds" into the sample sufficiently to obscure the peaks of interest (n-Alkanes) during chromatographic analysis. This first problem was solved by replacing the gasket material with glass-impregnated teflon. This material does not "bleed" into sample air. Once a cleanup procedure of back-flushing of the denuder with nitrogen at 200°C was complete, the denuder evidenced little or no residual interference when a blank sample was desorbed and analyzed.

A second problem was encountered when the sampling assembly was used to collect atmospheric samples. After initial curing and exposure to the atmosphere for sample collection, all subsequent thermal desorption samples yielded GC chromatograms with high levels of interference, even when sampling was preceded by several hours of nitrogen flushing. An example of this is given in Figure 19. The two most plausible explanations for this are as follows:

(1) Oxygen that is allowed to enter the denuder core is adsorbed by the Tenax and/or the adhesive coating, and reacts upon heating to form volatile oxides that are transferred to the GC

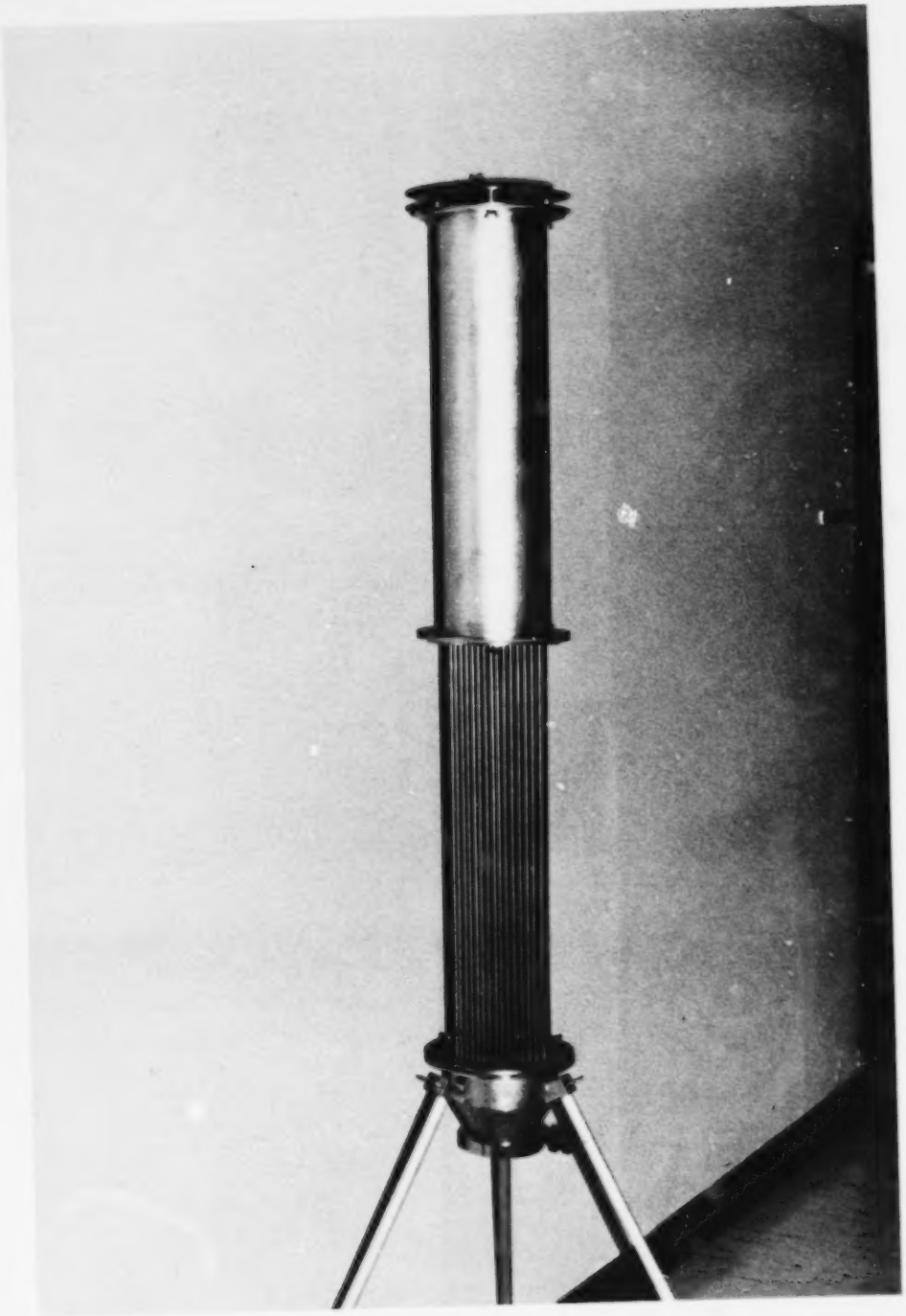

FIGURE 16 FULL SAMPLING ASSEMBLY

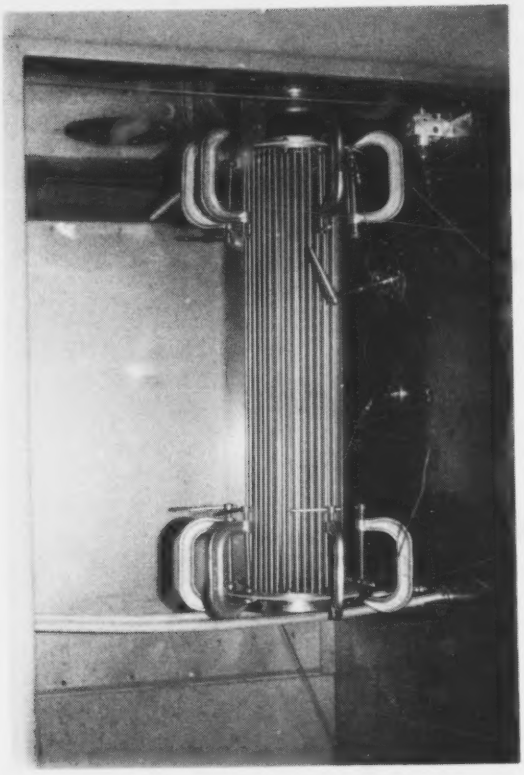

FIGURE 17a DENUDER MOUNTED IN OVEN FOR DESORPTION

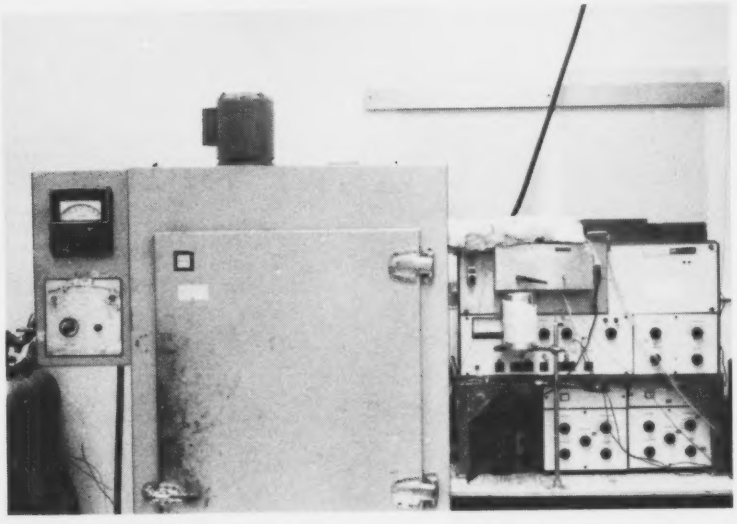

FIGURE 17b OVEN AND GAS CHROMATOGRAPH USED FOR SAMPLE ANALYSIS

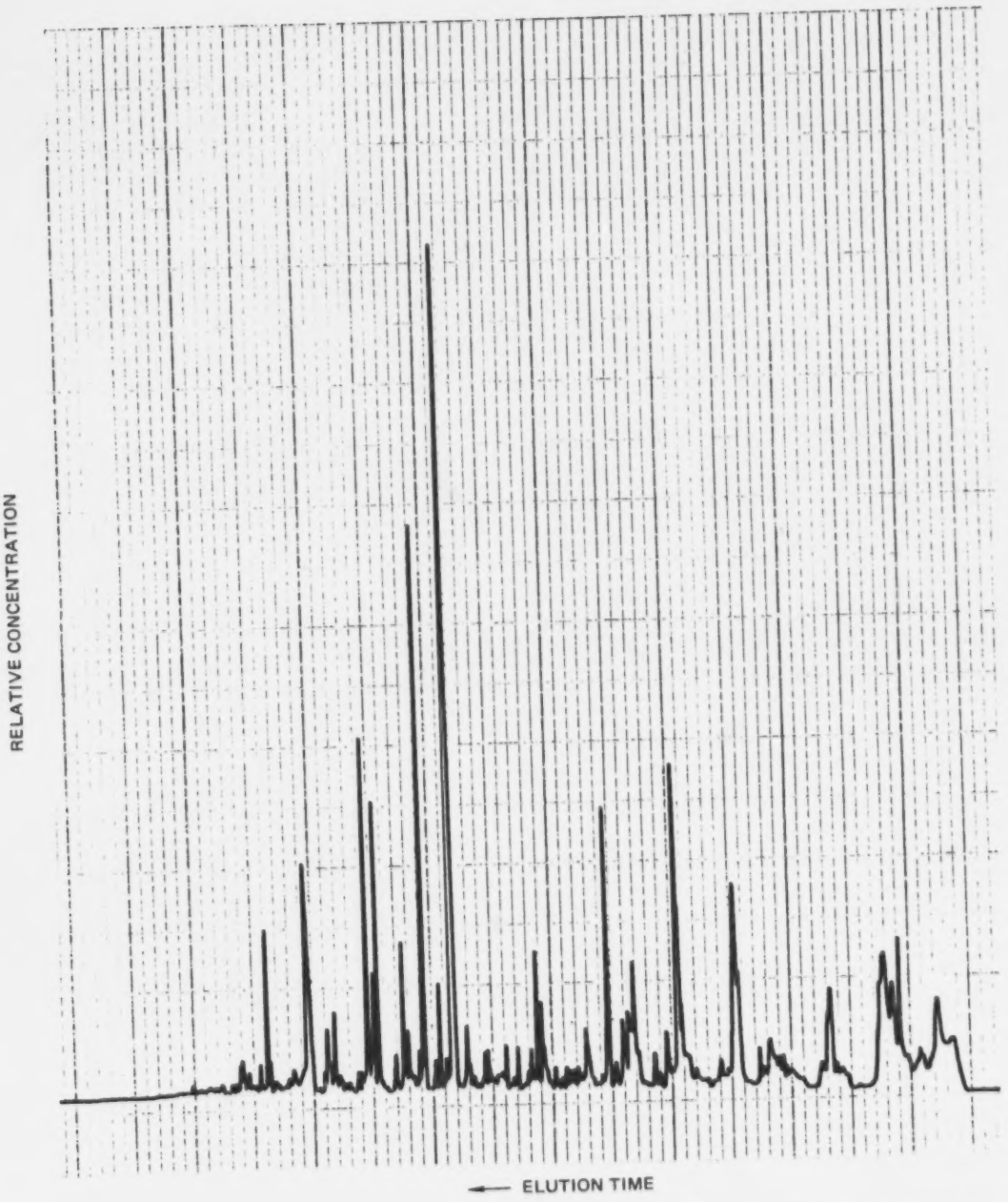

FIGURE 18 DESORPTION GC ANALYSIS TRACE OF COMPLETE DENUDER ASSEMBLY UPON COMPLETION OF HEAT CURING. TRACE SHOWS A LOW LEVEL OF INTERFERENTS.

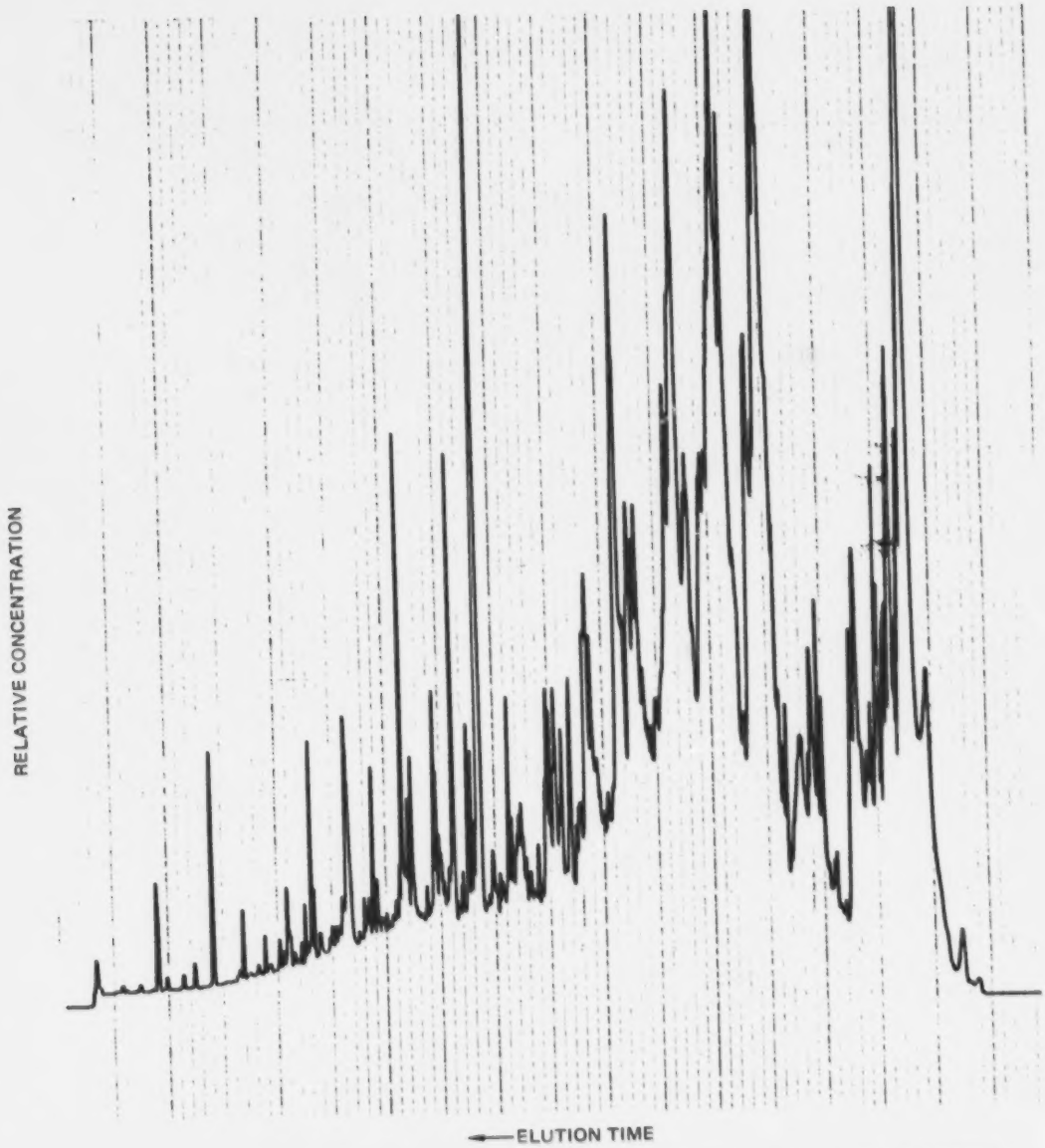

FIGURE 19 DESORPTION GC ANALYSIS TRACE OF 30 MIN. ATMOSPHERIC SAMPLE COLLECTED USING COMPLETE DENUDER ASSEMBLY. INTERFERENCE PRECLUDES ANALYZING TRACE FOR PRESENCE OF n-ALKANES.

column. The implications of this are serious since the denuder is exposed to oxygen during any atmospheric sampling, and heating is necessary for sample transfer to the GC. If oxygen is adsorbed on the tube walls, cold flushing is of limited help in removing it.

(2) The interference may be due to the transfer of water from the denuder to the GC after exposure of the denuder core to the atmosphere. The presence of early eluting interference in GC samples from the adhesive-coated single tubes during preliminary testing lead to the suspicion that the coating may be hygroscopic to some degree. Drying of the denuder sample was attempted after atmospheric exposure by heating the assembly to 100°C with nitrogen purging for 120 min. before further heating and sample collection. This drying step yielded little improvement.

The Tenax-GC adsorbent should not contribute to these two suspected problems. It was selected specifically because of its hydrophobic and thermal desorption properties. Interference may be the indirect result of inadequate flushing of the denuder assembly after exposure to air. The flow of the flush and desorption gas is restricted by the 1/16" tube fittings and attached tubing on the end caps. The achievable flow rate is more than enough to accommodate cryogenic trapping of the desorption gas flow, but may be inadequate for flushing the denuder tubes. Choosing to increase the flush time rather than the flow rate, particularly at an elevated temperature, could result in the undesirable interference effects in analyte desorption. This may not have been noticed in the case of the single tubes because flow rates through the tubes during flushing were higher.

Following the tests for background interference, the denuder was tested for its ability to quantitatively transfer n-Alkanes at the thermal desorption temperature. Mixtures of n-Alkanes were introduced into the transfer gas stream upstream of the denuder while the denuder and transfer line were heated to the temperature used for thermal desorption. The transfer gas was cryogenically trapped for 90 min. at a flow rate of 1000 ml/min. These chromatograms were compared with samples generated with the denuder removed from the gas line. The difference between the two sets of samples represents the retention or

retardation of the analytes in the hot denuder. Table 2 presents the direct transfer of each alkane through the denuder, expressed as a percentage of the amounts transferred without the denuder. It is apparent from the table that immediate transmission of alkanes through the hot denuder is low for some of the analyte range tested. Some of the higher molecular weight species were not transferred at all. Furthermore, a second sampling of the transfer gas following the first trapping period revealed the continued emission of medium and higher weight alkanes. In its present configuration, therefore, the denuder does not rapidly transfer these alkanes in a quantitative manner.

Table 2

SHORT TERM TRANSFER OF n-ALKANES THROUGH
DENUDER OPERATED AT DESORPTION TEMPERATURES

Carbon No.	n-Alkane Transfer %
10	70
11	75
12	103
13	99
14	104
15	94
16	34
17	7
18 through 24	0

In correcting this problem, attention must be given to the flushing flow rate. This was a factor in the interference problem, and may also affect sample transfer to the GC. Though the flow through the cryogenic trap has been maximized, the velocity of the flush gas through each of the 163 tubes in the denuder is only 0.3 cm/sec. Flushing of the tubes

under these conditions may be ineffective when compared to vapor diffusion rates. In its present configuration and thermal limitations, sample vapors may not be flash desorbed, but seem to be chromatographing through the denuder tubes as though through wall-coated open tubular GC columns. Such vapor flow through the tubes is likely to be retarded by continuous vapor/sorbent interaction that is related to each alkane's boiling point. Subsequent vapor transfer may be particularly slow for analytes with boiling points significantly above the desorption temperature. The consequence of this "denuder chromatography" is that each alkane homolog will elute at a different time, depending upon its retardation factor. Individual homologs can probably be effectively collected if their retention properties are understood.

Considering both the transfer and retention problems, quantitative collection and recovery of a range of LVO compounds (given the present experimental conditions) may not be practicable. The device, however, remains an effective denuder, and can be used to provide a sample of the aerosol fraction of an LVO. Comparison with a concurrent total sampling method such as that used by Duce and Gagosian (1982) would permit determination of the vapor fraction, and hence the aerosol/vapor fraction in the collected sample. Time and budget did not permit us to develop such a procedure, nor did it permit employment of an effective post filter LVO trap.

V CONCLUSIONS

Based on the atmospheric measurements of Broddin et al (1980) and Van Vaeck et al (1984), n-Alkanes in the atmosphere are predominantly in the vapor phase for carbon numbers less than 18. This varies seasonally somewhat. In the summer, atmospheric n-Alkanes up to carbon number 20 are predominantly in the vapor phase.

The assertions in the previous paragraph are supported by application of the analysis of Junge (1977) based on the BET theory of adsorption. When care is taken to obtain accurate estimates of the parameters used in the BET theory, almost exact correspondence with atmospheric measurements is achieved. The critical parameters used in estimating atmospheric aerosol/vapor phase distributions are the mean temperature for the period of interest and the atmospheric aerosol surface concentration. The former is season-dependent while the latter is, for the most part, dependent on the locale where the LVO aerosol/vapor is dispersed in the atmosphere.

As a sample collection system, the SRI sampling system performs as designed. The impactor inlet provides a clean preselection cut of the sample aerosol fraction at 10 μm, and the denuder adsorbs the n-Alkane test compounds vapor while passing aerosol with less than 2 percent loss. The adsorption of compounds from the atmosphere, however, is not selective so that when an attempt is made to recover the adsorbed sample by thermal desorption of the denuder, extraneous compounds (as evidenced by gas chromatographic analysis) completely obscure the compounds of interest. This occurs even when high concentrations of test vapor have been introduced into the atmospheric sample. The extraneous compounds may also cause changes in the elution times so that transferring a specific compound peak to a mass spectrometer on the basis of elution time is doubtful. Limiting sample collection time or dilution of the desorbed vapor sample does not improve the sample analysis conditions sufficiently to warrant using the denuder-derived sample to analyze for LVO in the atmosphere. Further improvements in the adhesive material

and additional tests are required before this system can be satisfactorily employed in field studies.

VI RECOMMENDATION SUMMARY

This study has indicated four areas in which further work is necessary before the original objectives of the study can be realized. These are discussed in the following subsections.

(1) If the BET-based phase distribution estimator is to be used for other LVO compounds, adsorption isotherms must be measured using suitable aerosol surfaces. From such isotherms, the BET parameters used in the phase calculations can be extracted. This information is not generally available in the literature except for limited families of compounds such as the n-Alkanes.

(2) Two questions can be raised based on the results reported from this work. First, why do BET adsorption parameters derived from adsorption isotherms of n-Alkanes adsorbed on an aerosolized carbon black surface seem to work in estimations of the phase distributions of the LVOs in the atmosphere? Second, atmospheric aerosols have some surface characteristics in common with carbon aerosol? These questions need further research if the adsorption of atmospheric organics on atmospheric aerosol surfaces is to be better understood.

(3) As noted above, several LVO compounds have no published adsorption information. For these compounds it may be necessary to develop a general formalism to calculate BET adsorption parameters. Ideally, the formalism would be used for any combination of LVO compound and aerosol adsorption surface. Development of such a form would require theoretical calculations based on current adsorption theories, and validation using measured adsorption isotherms.

(4) Based on our findings in laboratory tests of the denuder, it is evident that modifications of the denuder and/or desorption procedures are prerequisite to its effective use as an atmospheric LVO sample collector. Future research should include further testing with sorbent coatings to improve the thermal transfer properties, and reduce the trapping of possible interferents such as water. An ideal coating would be hydrophobic and would tolerate higher desorption temperatures than Tenax. Also, if the observed interferences were caused by the presence of oxygen or water, simple modifications can be made to the end caps of the denuder desorption assembly to allow a larger flush gas flow-rate and thus, more effective flushing of the denuder tubes.

The transfer of sample vapors can also be improved by increasing the transfer gas flow rate. However, this can only be accomplished with the incorporation of a device so that the cryogenic trap is sampling only a portion of the desorption stream. Alternatively, reducing the number of tubes in the denuder would increase the velocity of flush gas, and thus increase the flushing transfer efficiency. Both of these approaches would reduce the amount of interferents that are transferred to the cryogenic trap. However, it must also reduce the sensitivity of the sampler proportionately.

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Appendix A

AEROSOL/VAPOR PHASE CALCULATIONS FOR THE n-ALKANES

APPENDIX

The following Tables present the results of the aerosol/vapor phase calculations for the n-Alkanes discussed in Section III. Aerosol/total phase fractions are calculated for three seasonal regimes--Winter, Spring/Fall and Summer--by assuming a mean temperature for each, i.e.:

Season	Temperature (°K)
Winter	275
Spring/Fall	290
Summer	300

For each temperature, calculations were done for three locales--Urban, Rural and Remote--by assuming an atmospheric aerosol surface concentration for each locale, i.e.:

Locale	Aerosol Surface $\mu m^2/cm^3$
Urban	1×10^{-5}
Rural	2×10^{-6}
Remote	3×10^{-7}

Aerosol fractions (Fa) for each season and locale are given in Tables A-1 through A-9 for the n-Alkanes with carbon numbers 10 through 28. Also given are the vapor pressures (Po), Kelvin correction, and surface energy terms (c) used in the calculations.

Table A1

FRACTION OF n-ALKANES IN THE AEROSOL PHASE (f_a) AS A FUNCTION OF CARBON NUMBER FOR AN URBAN BACKGROUND AEROSOL IN WINTER, i.e. AEROSOL SURFACE CONCENTRATION = 1.000E-05, $\mu m^2/cm^3$ AND TEMPERATURE = 275 °K

Carbon No.	Molecular Weight (M)	Vapor Pressure (P_o) (Torr)	Kelvin Correction	P_oM (torr gm/mole)	C	f_a
10	142	3.78E-01	1.03E+00	5.56E+01	1.59E+02	1.52E-05
11	156	1.37E-01	1.04E+00	2.22E+01	2.09E+02	5.01E-05
12	170	5.36E-02	1.04E+00	9.51E+00	2.75E+02	1.54E-04
13	184	1.48E-02	1.05E+00	2.85E+00	3.62E+02	6.76E-04
14	198	5.05E-03	1.05E+00	1.05E+00	4.77E+02	2.40E-03
15	212	1.56E-03	1.06E+00	3.50E-01	6.28E+02	9.44E-03
16	226	5.20E-04	1.07E+00	1.25E-01	8.26E+02	3.39E-02
17	240	2.79E-04	1.07E+00	7.18E-02	1.09E+03	7.45E-02
18	254	2.22E-04	1.08E+00	6.08E-02	1.43E+03	1.11E-01
19	268	6.15E-05	1.09E+00	1.79E-02	1.88E+03	3.59E-01
20	282	1.62E-05	1.09E+00	4.98E-03	2.48E+03	7.26E-01
21	296	1.05E-05	1.10E+00	3.43E-03	3.26E+03	8.35E-01
22	310	2.13E-06	1.11E+00	7.33E-04	4.29E+03	9.69E-01
23	324	1.74E-06	1.12E+00	6.29E-04	5.64E+03	9.79E-01
24	338	6.33E-07	1.12E+00	2.41E-04	7.42E+03	9.94E-01
25	352	1.57E-07	1.13E+00	6.25E-05	9.77E+03	9.99E-01
26	366	5.41E-08	1.14E+00	2.26E-05	1.29E+04	1.00E+00
27	380	2.80E-08	1.15E+00	1.23E-05	1.69E+04	1.00E+00
28	394	2.46E-09	1.16E+00	1.13E-06	2.23E+04	1.00E+00

Table A2

FRACTION OF n-ALKANES IN THE AEROSOL PHASE (f_a) AS A FUNCTION OF CARBON NUMBER FOR A RURAL BACKGROUND AEROSOL IN WINTER, i.e. AEROSOL SURFACE CONCENTRATION = 2.000E-06, $\mu m^2/cm^3$ AND TEMPERATURE = 275 °K

Carbon No.	Molecular Weight (M)	Vapor Pressure (P_o) (Torr)	Kelvin Correction	P_oM (torr gm/mole)	C	f_a
10	142	3.78E-01	1.03E+00	5.56E+01	1.59E+02	3.05E-06
11	156	1.37E-01	1.04E+00	2.22E+01	2.09E+02	1.00E-05
12	170	5.36E-02	1.04E+00	9.51E+00	2.75E+02	3.08E-05
13	184	1.48E-02	1.05E+00	2.85E+00	3.62E+02	1.35E-04
14	198	5.05E-03	1.05E+00	1.05E+00	4.77E+02	4.81E-04
15	212	1.56E-03	1.06E+00	3.50E-01	6.28E+02	1.90E-03
16	226	5.20E-04	1.07E+00	1.25E-01	8.26E+02	6.97E-03
17	240	2.79E-04	1.07E+00	7.18E-02	1.09E+03	1.58E-02
18	254	2.22E-04	1.08E+00	6.08E-02	1.43E+03	2.44E-02
19	268	6.15E-05	1.09E+00	1.79E-02	1.88E+03	1.01E-01
20	282	1.62E-05	1.09E+00	4.98E-03	2.48E+03	3.46E-01
21	296	1.05E-05	1.10E+00	3.43E-03	3.26E+03	5.02E-01
22	310	2.13E-06	1.11E+00	7.33E-04	4.29E+03	8.62E-01
23	324	1.74E-06	1.12E+00	6.29E-04	5.64E+03	9.05E-01
24	338	6.33E-07	1.12E+00	2.41E-04	7.42E+03	9.70E-01
25	352	1.57E-07	1.13E+00	6.25E-05	9.77E+03	9.94E-01
26	366	5.41E-08	1.14E+00	2.26E-05	1.29E+04	9.98E-01
27	380	2.80E-08	1.15E+00	1.23E-05	1.69E+04	9.99E-01
28	394	2.46E-09	1.16E+00	1.13E-06	2.23E+04	1.00E+00

Table A3

FRACTION OF n-ALKANES IN THE AEROSOL PHASE (f_a) AS A FUNCTION OF CARBON NUMBER FOR A REMOTE BACKGROUND AEROSOL IN WINTER, i.e. AEROSOL SURFACE CONCENTRATION = 3.000E-07, $\mu m^2/cm^3$ AND TEMPERATURE = 275 °K

Carbon No.	Molecular Weight (M)	Vapor Pressure (P_o) (Torr)	Kelvin Correction	P_oM (torr gm/mole)	C	f_a
10	142	3.78E-01	1.03E+00	5.56E+01	1.59E+02	4.57E-07
11	156	1.37E-01	1.04E+00	2.22E+01	2.09E+02	1.50E-06
12	170	5.36E-02	1.04E+00	9.51E+00	2.75E+02	4.62E-06
13	184	1.48E-02	1.05E+00	2.85E+00	3.62E+02	2.03E-05
14	198	5.05E-03	1.05E+00	1.05E+00	4.77E+02	7.22E-05
15	212	1.56E-03	1.06E+00	3.50E-01	6.28E+02	2.86E-04
16	226	5.20E-04	1.07E+00	1.25E-01	8.26E+02	1.05E-03
17	240	2.79E-04	1.07E+00	7.18E-02	1.09E+03	2.41E-03
18	254	2.22E-04	1.08E+00	6.08E-02	1.43E+03	3.74E-03
19	268	6.15E-05	1.09E+00	1.79E-02	1.88E+03	1.65E-02
20	282	1.62E-05	1.09E+00	4.98E-03	2.48E+03	7.35E-02
21	296	1.05E-05	1.10E+00	3.43E-03	3.26E+03	1.32E-01
22	310	2.13E-06	1.11E+00	7.33E-04	4.29E+03	4.83E-01
23	324	1.74E-06	1.12E+00	6.29E-04	5.64E+03	5.89E-01
24	338	6.33E-07	1.12E+00	2.41E-04	7.42E+03	8.31E-01
25	352	1.57E-07	1.13E+00	6.25E-05	9.77E+03	9.61E-01
26	366	5.41E-08	1.14E+00	2.26E-05	1.29E+04	9.89E-01
27	380	2.80E-08	1.15E+00	1.23E-05	1.69E+04	9.95E-01
28	394	2.46E-09	1.16E+00	1.13E-06	2.23E+04	1.00E+00

Table A4

FRACTION OF n-ALKANES IN THE AEROSOL PHASE (f_a) AS A FUNCTION OF CARBON NUMBER FOR AN URBAN BACKGROUND AEROSOL IN SPRING/FALL, i.e. AEROSOL SURFACE CONCENTRATION = 1.000E-05, $\mu m^2/cm^3$ AND TEMPERATURE = 290 °K

Carbon No.	Molecular Weight (M)	Vapor Pressure (P_o) (Torr)	Kelvin Correction	P_oM (torr gm/mole)	C	f_a
10	142	1.06E+00	1.03E+00	1.56E+02	1.22E+02	4.40E-06
11	156	4.07E-01	1.04E+00	6.59E+01	1.59E+02	1.35E-05
12	170	1.65E-01	1.04E+00	2.92E+01	2.06E+02	3.95E-05
13	184	5.05E-02	1.05E+00	9.74E+00	2.67E+02	1.54E-04
14	198	1.86E-02	1.05E+00	3.87E+00	3.47E+02	5.02E-04
15	212	6.23E-03	1.06E+00	1.40E+00	4.50E+02	1.80E-03
16	226	2.23E-03	1.07E+00	5.38E-01	5.83E+02	6.05E-03
17	240	1.22E-03	1.07E+00	3.14E-01	7.57E+02	1.33E-02
18	254	9.58E-04	1.08E+00	2.62E-01	9.82E+02	2.06E-02
19	268	2.93E-04	1.09E+00	8.52E-02	1.27E+03	7.74E-02
20	282	7.97E-05	1.09E+00	2.46E-02	1.65E+03	2.74E-01
21	296	5.63E-05	1.10E+00	1.83E-02	2.14E+03	3.96E-01
22	310	1.17E-05	1.11E+00	4.01E-03	2.78E+03	7.95E-01
23	324	1.06E-05	1.12E+00	3.83E-03	3.61E+03	8.41E-01
24	338	4.06E-06	1.12E+00	1.54E-03	4.68E+03	9.44E-01
25	352	1.12E-06	1.13E+00	4.48E-04	6.07E+03	9.87E-01
26	366	4.18E-07	1.14E+00	1.75E-04	7.88E+03	9.96E-01
27	380	2.24E-07	1.15E+00	9.80E-05	1.02E+04	9.98E-01
28	394	2.42E-08	1.16E+00	1.11E-05	1.33E+04	1.00E+00

Table A5

FRACTION OF n-ALKANES IN THE AEROSOL PHASE (f_a) AS A FUNCTION OF CARBON NUMBER FOR A RURAL BACKGROUND AEROSOL IN SPRING/FALL, i.e. AEROSOL SURFACE CONCENTRATION = 2.000E-06, $\mu m^2/cm^3$ AND TEMPERATURE = 290 °K

Carbon No.	Molecular Weight (M)	Vapor Pressure (P_o) (Torr)	Kelvin Correction	P_oM (torr gm/mole)	C	f_a
10	142	1.06E+00	1.03E+00	1.56E+02	1.22E+02	8.80E-07
11	156	4.07E-01	1.04E+00	6.59E+01	1.59E+02	2.70E-06
12	170	1.65E-01	1.04E+00	2.92E+01	2.06E+02	7.91E-06
13	184	5.05E-02	1.05E+00	9.74E+00	2.67E+02	3.08E-05
14	198	1.86E-02	1.05E+00	3.87E+00	3.47E+02	1.00E-04
15	212	6.23E-03	1.06E+00	1.40E+00	4.50E+02	3.60E-04
16	226	2.23E-03	1.07E+00	5.38E-01	5.83E+02	1.22E-03
17	240	1.22E-03	1.07E+00	3.14E-01	7.57E+02	2.69E-03
18	254	9.58E-04	1.08E+00	2.62E-01	9.82E+02	4.18E-03
19	268	2.93E-04	1.09E+00	8.52E-02	1.27E+03	1.65E-02
20	282	7.97E-05	1.09E+00	2.46E-02	1.65E+03	7.02E-02
21	296	5.63E-05	1.10E+00	1.83E-02	2.14E+03	1.16E-01
22	310	1.17E-05	1.11E+00	4.01E-03	2.78E+03	4.37E-01
23	324	1.06E-05	1.12E+00	3.83E-03	3.61E+03	5.14E-01
24	338	4.06E-06	1.12E+00	1.54E-03	4.68E+03	7.73E-01
25	352	1.12E-06	1.13E+00	4.48E-04	6.07E+03	9.38E-01
26	366	4.18E-07	1.14E+00	1.75E-04	7.88E+03	9.81E-01
27	380	2.24E-07	1.15E+00	9.80E-05	1.02E+04	9.92E-01
28	394	2.42E-08	1.16E+00	1.11E-05	1.33E+04	9.99E-01

Table A6

FRACTION OF n-ALKANES IN THE AEROSOL PHASE (f_a) AS A FUNCTION OF CARBON NUMBER FOR A REMOTE BACKGROUND AEROSOL IN SPRING/FALL, i.e. AEROSOL SURFACE CONCENTRATION = 3.000E-07, $\mu m^2/cm^3$ AND TEMPERATURE = 290 °K

Carbon No.	Molecular Weight (M)	Vapor Pressure (P_o) (Torr)	Kelvin Correction	P_oM (torr gm/mole)	C	f_a
10	142	1.06E+00	1.03E+00	1.56E+02	1.22E+02	1.32E-07
11	156	4.07E-01	1.04E+00	6.59E+01	1.59E+02	4.05E-07
12	170	1.65E-01	1.04E+00	2.92E+01	2.06E+02	1.19E-06
13	184	5.05E-02	1.05E+00	9.74E+00	2.67E+02	4.61E-06
14	198	1.86E-02	1.05E+00	3.87E+00	3.47E+02	1.51E-05
15	212	6.23E-03	1.06E+00	1.40E+00	4.50E+02	5.41E-05
16	226	2.23E-03	1.07E+00	5.38E-01	5.83E+02	1.83E-04
17	240	1.22E-03	1.07E+00	3.14E-01	7.57E+02	4.05E-04
18	254	9.58E-04	1.08E+00	2.62E-01	9.82E+02	6.29E-04
19	268	2.93E-04	1.09E+00	8.52E-02	1.27E+03	2.51E-03
20	282	7.97E-05	1.09E+00	2.46E-02	1.65E+03	1.12E-02
21	296	5.63E-05	1.10E+00	1.83E-02	2.14E+03	1.93E-02
22	310	1.17E-05	1.11E+00	4.01E-03	2.78E+03	1.04E-01
23	324	1.06E-05	1.12E+00	3.83E-03	3.61E+03	1.37E-01
24	338	4.06E-06	1.12E+00	1.54E-03	4.68E+03	3.38E-01
25	352	1.12E-06	1.13E+00	4.48E-04	6.07E+03	6.95E-01
26	366	4.18E-07	1.14E+00	1.75E-04	7.88E+03	8.84E-01
27	380	2.24E-07	1.15E+00	9.80E-05	1.02E+04	9.46E-01
28	394	2.42E-08	1.16E+00	1.11E-05	1.33E+04	9.95E-01

Table A7

FRACTION OF n-ALKANES IN THE AEROSOL PHASE (f_a) AS A FUNCTION OF CARBON NUMBER FOR AN URBAN BACKGROUND AEROSOL IN SUMMER, i.e. AEROSOL SURFACE CONCENTRATION = 1.000E-05, $\mu m^2/cm^3$ AND TEMPERATURE = 300 °K

Carbon No.	Molecular Weight (M)	Vapor Pressure (P_o) (Torr)	Kelvin Correction	P_oM (torr gm/mole)	C	f_a
10	142	2.00E+00	1.03E+00	2.93E+02	1.04E+02	2.06E-06
11	156	7.91E-01	1.04E+00	1.28E+02	1.34E+02	6.08E-06
12	170	3.27E-01	1.04E+00	5.80E+01	1.72E+02	1.73E-05
13	184	1.07E-01	1.05E+00	2.07E+01	2.22E+02	6.23E-05
14	198	4.11E-02	1.05E+00	8.58E+00	2.85E+02	1.93E-04
15	212	1.45E-02	1.06E+00	3.26E+00	3.67E+02	6.52E-04
16	226	5.44E-03	1.07E+00	1.31E+00	4.72E+02	2.08E-03
17	240	3.02E-03	1.07E+00	7.76E-01	6.07E+02	4.52E-03
18	254	2.34E-03	1.08E+00	6.41E-01	7.81E+02	7.02E-03
19	268	7.60E-04	1.09E+00	2.21E-01	1.00E+03	2.57E-02
20	282	2.12E-04	1.09E+00	6.52E-02	1.29E+03	1.03E-01
21	296	1.57E-04	1.10E+00	5.10E-02	1.66E+03	1.59E-01
22	310	3.30E-05	1.11E+00	1.13E-02	2.14E+03	5.22E-01
23	324	3.19E-05	1.12E+00	1.15E-02	2.75E+03	5.80E-01
24	338	1.26E-05	1.12E+00	4.81E-03	3.53E+03	8.10E-01
25	352	3.74E-06	1.13E+00	1.49E-03	4.54E+03	9.46E-01
26	366	1.46E-06	1.14E+00	6.10E-04	5.84E+03	9.82E-01
27	380	7.96E-07	1.15E+00	3.49E-04	7.52E+03	9.92E-01
28	394	9.78E-08	1.16E+00	4.48E-05	9.67E+03	9.99E-01

Table A8

FRACTION OF n-ALKANES IN THE AEROSOL PHASE (f_a) AS A FUNCTION OF CARBON NUMBER FOR A RURAL BACKGROUND AEROSOL IN SUMMER, i.e. AEROSOL SURFACE CONCENTRATION = 2.000E-06, $\mu m^2/cm^3$ AND TEMPERATURE = 300 °K

Carbon No.	Molecular Weight (M)	Vapor Pressure (P_o) (Torr)	Kelvin Correction	P_oM (torr gm/mole)	C	f_a
10	142	2.00E+00	1.03E+00	2.93E+02	1.04E+02	4.13E-07
11	156	7.91E-01	1.04E+00	1.28E+02	1.34E+02	1.22E-06
12	170	3.27E-01	1.04E+00	5.80E+01	1.72E+02	3.45E-06
13	184	1.07E-01	1.05E+00	2.07E+01	2.22E+02	1.25E-05
14	198	4.11E-02	1.05E+00	8.58E+00	2.85E+02	3.86E-05
15	212	1.45E-02	1.06E+00	3.26E+00	3.67E+02	1.30E-04
16	226	5.44E-03	1.07E+00	1.31E+00	4.72E+02	4.18E-04
17	240	3.02E-03	1.07E+00	7.76E-01	6.07E+02	9.07E-04
18	254	2.34E-03	1.08E+00	6.41E-01	7.81E+02	1.41E-03
19	268	7.60E-04	1.09E+00	2.21E-01	1.00E+03	5.24E-03
20	282	2.12E-04	1.09E+00	6.52E-02	1.29E+03	2.25E-02
21	296	1.57E-04	1.10E+00	5.10E-02	1.66E+03	3.64E-02
22	310	3.30E-05	1.11E+00	1.13E-02	2.14E+03	1.79E-01
23	324	3.19E-05	1.12E+00	1.15E-02	2.75E+03	2.16E-01
24	338	1.26E-05	1.12E+00	4.81E-03	3.53E+03	4.60E-01
25	352	3.74E-06	1.13E+00	1.49E-03	4.54E+03	7.79E-01
26	366	1.46E-06	1.14E+00	6.10E-04	5.84E+03	9.17E-01
27	380	7.96E-07	1.15E+00	3.49E-04	7.52E+03	9.62E-01
28	394	9.78E-08	1.16E+00	4.48E-05	9.67E+03	9.96E-01

Table A9

FRACTION OF n-ALKANES IN THE AEROSOL PHASE (f_a) AS A FUNCTION OF CARBON NUMBER FOR A REMOTE BACKGROUND AEROSOL IN SUMMER, i.e. AEROSOL SURFACE CONCENTRATION = 3.000E-07, $\mu m^2/cm^3$ AND TEMPERATURE = 300 °K

Carbon No.	Molecular Weight (M)	Vapor Pressure (P_o) (Torr)	Kelvin Correction	P_oM (torr gm/mole)	C	f_a
10	142	2.00E+00	1.03E+00	2.93E+02	1.04E+02	6.19E-08
11	156	7.91E-01	1.04E+00	1.28E+02	1.34E+02	1.82E-07
12	170	3.27E-01	1.04E+00	5.80E+01	1.72E+02	5.18E-07
13	184	1.07E-01	1.05E+00	2.07E+01	2.22E+02	1.87E-06
14	198	4.11E-02	1.05E+00	8.58E+00	2.85E+02	5.79E-06
15	212	1.45E-02	1.06E+00	3.26E+00	3.67E+02	1.96E-05
16	226	5.44E-03	1.07E+00	1.31E+00	4.72E+02	6.27E-05
17	240	3.02E-03	1.07E+00	7.76E-01	6.07E+02	1.36E-04
18	254	2.34E-03	1.08E+00	6.41E-01	7.81E+02	2.12E-04
19	268	7.60E-04	1.09E+00	2.21E-01	1.00E+03	7.90E-04
20	282	2.12E-04	1.09E+00	6.52E-02	1.29E+03	3.44E-03
21	296	1.57E-04	1.10E+00	5.10E-02	1.66E+03	5.63E-03
22	310	3.30E-05	1.11E+00	1.13E-02	2.14E+03	3.17E-02
23	324	3.19E-05	1.12E+00	1.15E-02	2.75E+03	3.98E-02
24	338	1.26E-05	1.12E+00	4.81E-03	3.53E+03	1.13E-01
25	352	3.74E-06	1.13E+00	1.49E-03	4.54E+03	3.46E-01
26	366	1.46E-06	1.14E+00	6.10E-04	5.84E+03	6.25E-01
27	380	7.96E-07	1.15E+00	3.49E-04	7.52E+03	7.89E-01
28	394	9.78E-08	1.16E+00	4.48E-05	9.67E+03	9.74E-01